

Supporting Information

Feedstocks to Pharmacophores: Cu-Catalyzed Oxidative Arylation of Inexpensive Alkylarenes Enabling Direct Access to Diarylalkanes

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I. General Considerations

All reagents were purchased and used as received unless otherwise noted. Cu salts were purchased from Aldrich. Boronic acids and C–H substrates were purchased from Oakwood, Combi-Blocks, Chem-Impex, or Aldrich. Ligands were purchased from Aldrich. 2-Methyl-2,4-pentanediol was purchased from TCI America. Toluene was used from a solvent system dried by molecular sieves. All peroxides and oxidants were used as received from Aldrich and Combi-Blocks. In the experimental section, “readily purchasable” refers to availability from a vendor for less than \$500.00 per gram, without a special order.

All coupling reactions were set up in an LC Technology Solutions nitrogen-filled glovebox, except where specifically noted. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 spectrometer or a Bruker 500 spectrometer and chemical shifts are reported in parts per

million (ppm), referenced to CDCl₃ at 7.26 ppm (¹H) and 77.16 (¹³C). Chromatography was performed using an automated Biotage Isolera® with reusable 120g or 60g Biotage® SNAP Ultra C-18 cartridges or standard silica cartridges. High-resolution mass spectra were obtained using a Thermo Q Exactive™ Plus via (ASAP-MS) by the mass spectrometry facility at the University of Wisconsin (funded by NIH grant: 1S10OD020022-1). GC analyses were performed on a Shimadzu gas chromatograph (GC-2010 Plus) using a Phenomenex® Zebron™ ZB-Wax capillary column (30 m x 0.25 mm x 0.25 μm film thickness).

II. General Procedure for 2-Aryl-4,4,6-trimethyl-1,3,2-dioxaborinane (ArBdiol) Synthesis

Set-up: To a 15 mL vial was added boronic acid (1 equiv.), 2-methyl-2,4-pentanediol (1.1 equiv.), and dichloromethane (0.5 M). The reaction was then capped and stirred for 16 h at r.t.

Work-up: The reaction mixture was washed 1x with saturated NaHCO₃, and the aqueous phase was then extracted with dichloromethane. The organics were combined and washed 1x with saturated NaHCO₃ and 1x with brine. After washing, the organics were combined, dried with MgSO₄, and concentrated to afford the product. Products showing discoloration were passed through a silica plug with 90% pentane/Et₂O to remove trace impurities. If a precipitate formed from the pentane/Et₂O, the precipitate was filtered, and either the filtered material or filtrate was isolated as the product (without further purification).

III. General Procedure for Cu-Catalyzed Intermolecular Methylarene C–H Arylation

Set-up: In a nitrogen-filled glovebox, a disposable 15 mL glass vial was charged with CuI•DMS complex (0.015 mmol, 3.6 mg, 0.03 equiv.), 1,10-phenanthroline (0.075 mmol, 13.5 mg, 0.15 equiv.), the requisite aryl dioxaborinane (0.5 mmol, 1.0 equiv.), the methyl arene coupling partner (1.6 mL, 0.3 M), di-*tert*-butyl peroxide (2.0 mmol, 366 μL, 4.0 equiv.), and a Teflon stir bar. The vial was then capped with a PTFE-lined pierceable cap and removed from the glovebox. After taping the cap with electrical tape, the vial was placed in an aluminum heating block on a heated stir plate, and the mixture was stirred at 90 °C for 48 h.

Work-up: At the end of the reaction, the mixture turned a red/brown color. The vial was then removed from the heat/stir plate and allowed to cool to room temperature. Dibromomethane was then added via syringe as ¹H NMR internal standard (0.5 mmol, 35 μL, 1 equiv.), and an aliquot of the reaction mixture was taken for analysis by ¹H NMR to determine the calibrated yield. The reaction was then condensed by rotary evaporation (taking care not to remove the desired product). The methyl arene starting material is sometimes removed in this step. The crude reaction mixture was then diluted with 100:1 pentane:EtOAc and a portion of it was passed over a silica plug, yielding a colorless or red/yellow solution (for normal phase columns, the crude reaction mixture was instead diluted with 9:1 pentane:EtOAc and then filtered over a syringe filter). The pentane:EtOAc was removed by rotary evaporation, and the mixture was then purified using automated reverse phase column chromatography (Biotage; MeOH/H₂O with 0.1% TFA gradient; DCM was used to load the sample) or automated normal phase column chromatography (Biotage; pentane:EtOAc gradient). For reverse phase columns, the purified product fractions were collected and extracted 2x with 9:1 pentane:Et₂O and brine. These organic layers were collected, dried by MgSO₄, and the solvent was removed to yield the desired 1,1-diarylmethane.

IV. General Procedure for Cu-Catalyzed Intermolecular Alkyl Arene C–H Arylation

Set-up: In a nitrogen-filled glovebox, a disposable 15 mL glass vial was charged with either 5 or 3 mol% CuI•DMS complex (0.025 mmol, 6.0 mg, 0.05 equiv. or 0.015 mmol, 3.6 mg, 0.03 equiv.), 1,10-phenanthroline or 1,10-phenanthroline-5,6-dione ligand (0.075 mmol, 13.5 mg or 15.8 mg respectively, 0.15 equiv.), the requisite aryl dioxaborinane (0.5 mmol, 1.0 equiv.), the alkyl arene coupling partner (5 mmol, 10.0 equiv.), di-*tert*-butyl peroxide (2.0 mmol, 366 μ L, 4.0 equiv.), chlorobenzene solvent (313 μ L, 1.6 M), and a Teflon stir bar. The vial was then capped with a PTFE-lined pierceable septum cap and removed from the glovebox. After taping the cap with electrical tape, the vial was placed on an aluminum heating block on a heated stir plate, and the reaction mixture was stirred at 90 °C for 48 h.

Work-up: Identical to that in III. Reactions sometimes needed to be filtered with a syringe filter before they are passed through the silica plug with 100:1 pentane:EtOAc (particularly for the 1-chloro-3-phenylpropane substrates).

V. Procedure for Glovebox-Free Cu-Catalyzed Benzylic C–H Arylation of 4-Ethylanisole

Set-up: In a fume hood, a disposable 24 mL glass vial was charged with CuI•DMS complex (12.3 mg, 0.051 mmol, 0.03 equiv.), 1,10-phenanthroline-5,6-dione (53.7 mg, 0.255 mmol, 0.15 equiv.), 2-(3,4,5-methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (500 mg, 1.7 mmol, 1.0 equiv.), 4-ethylanisole (2.4 mL, 17 mmol, 10.0 equiv.), di-*tert*-butyl peroxide (1.2 mL, 6.8 mmol, 4.0 equiv.), chlorobenzene solvent (1 mL, 1.6 M), and a Teflon stir bar. The vial was then capped with a PTFE-lined pierceable septum cap and taped with electrical tape. The septum was pierced and the vial was evacuated and then backfilled with N₂ three times (evacuate/backfill quickly or freeze-pump-thaw to avoid bumping). It was then placed on an aluminum heating block on a heated stir plate and stirred at 90 °C for 24 h.

Work-up: Identical to that in III., except dichloromethane was used as the eluent for the silica plug. This product was isolable using normal-phase flash chromatography. The first several fractions of the column contained pure 4-ethylanisole starting material (76% of the unreacted starting material, i.e. 12 mmol of 15.81 mmol, was recovered)



Glovebox-free reaction after 24 h.

VI. Screening Tables

A) Nucleophile Screening Table

| entry | Ph-[M] | % yield ^a |
|-------|-------------------|----------------------|
| 1 | | 76 |
| 2 | | 61 |
| 3 | | 1 |
| 4 | w/ 1 equiv. NaOMe | 3 |
| 5 | | 2 |
| 6 | | 0 |
| 7 | | 0 |
| 8 | | 0 |
| 9 | | 2 |
| 10 | w/ 1 equiv. NaOMe | 13 |
| 11 | | 6 |
| 12 | w/ 1 equiv. CsF | 3 |

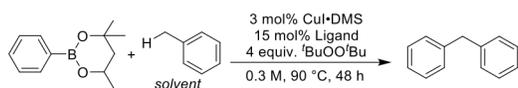
^aReactions run on 0.4 mmol scale and yields analyzed by calibrated GC using 1 eq. tetradecane as an internal standard.

B) Copper Source Screening Table

| entry | Cu Source | % yield ^a |
|-------|-----------|----------------------|
| 1 | CuI•DMS | 76 |
| 2 | CuI | 74 |
| 3 | CuBr•DMS | 67 |
| 4 | CuBr | 73 |
| 5 | CuCl | 61 |
| 6 | CuCN | 69 |

^aReactions run on 0.4 mmol scale and yields analyzed by calibrated GC using 1 eq. tetradecane as an internal standard.

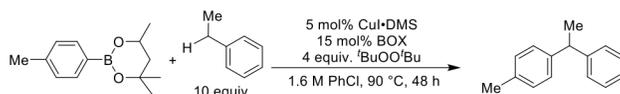
C) Ligand Screening Table



| entry | Ligand | % yield ^a |
|-------|--------|----------------------|
| 1 | | 76 |
| 2 | | 29 ^b |
| 3 | | 23 |
| 4 | | 55 |
| 5 | | 8 |
| 6 | | 32 |
| 7 | | 4 |
| 8 | | 3 |

^aReactions run on 0.4 mmol scale and yields analyzed by calibrated GC using 1 eq. tetradecane as an internal standard. ^bAffords a 60% yield if 4 mol% Cu and 12 mol% phd are used rather than 3 mol% and 15 mol%.

D) Chiral Ligand Screening



| entry | Box Ligand | % yield ^a |
|-------|------------|----------------------|
| 1 | | 1 |
| 2 | | 8 |
| 3 | | 0 |
| 4 | | 11 |
| 5 | | 0 |

^aReactions run on 0.4 mmol scale and yields analyzed by ¹H NMR with 1 eq. CH₂Br₂ as the internal standard.

E) Oxidant Screening Table

| entry | Oxidant | % yield ^a |
|-------|--|----------------------|
| 1 | ^t BuOO ^t Bu | 76 |
| 2 | ^t BuOOH (6 M in decane) | 10 |
| 3 | ^t BuOOBz | 3 |
| 4 | | 24 |
| 5 | | 3 |
| 6 | Oxone | 2 |
| 7 | | 2 |
| 8 | K ₂ S ₂ O ₈ | 2 |

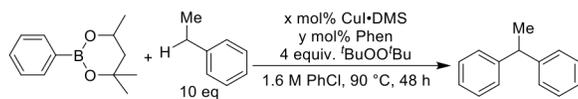
^aReactions run on 0.4 mmol scale and yields analyzed by calibrated GC using 1 eq. tetradecane as an internal standard.

F) Control Reactions (Temperature, Time, Air, Concentration, Catalyst)

| entry | Variation to Conditions | % yield ^a |
|-------|---|----------------------|
| 1 | 70 °C instead of 90 °C | 22 |
| 2 | 24 h instead of 48 h | 76 ^b |
| 3 | Set up on bench under air | 60 ^c |
| 4 | 10 eq. Toluene, Same Volume (0.43 mL Toluene + 0.87 mL PhCl) | 35 ^d |
| 5 | No CuI·DMS | 5 |
| 6 | No phen | 4 |
| 7 | No Oxidant | 0 |
| 8 | No Nucleophile | 0 |
| 9 | 1 eq. Product Added at Start (no PhBDiol) | 77 |

^aReactions run on 0.4 mmol scale and yields analyzed by calibrated GC using 1 eq. tetradecane as an internal standard. ^bIn this screen, the 48h reaction gave 80% yield by GC. ^cComponents weighed out on bench, and then capped. ^dSee caption in table F for better conditions with 10 equiv.

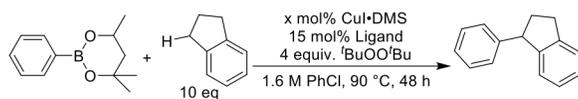
G) Ethyl Benzene Optimization of Ligand/Cu Ratio



| entry | mol% Ligand | mol% Cu | Ligand:Cu Ratio | % yield ^a |
|----------|-------------|----------|-----------------|------------------------|
| 1 | 10 | 5 | 2 | 52% |
| 2 | 12 | 4 | 3 | 66% |
| 3 | 15 | 5 | 3 | 68%^b |
| 4 | 30 | 10 | 3 | 64% |
| 5 | 20 | 5 | 4 | 52% |

^aReactions run on 0.4 mmol scale and yields analyzed by calibrated GC using 1 eq. tetradecane as an internal standard. ^b63% yield using toluene as the C-H substrate.

H) Alkyl Arene (Indane) Optimized Conditions w/ phd



| entry | Ligand | mol% Cu | Ligand:Cu Ratio | % yield ^a |
|----------|------------|----------|-----------------|----------------------|
| 1 | Phen | 5 | 3 | 45% |
| 2 | Phen | 3 | 5 | 52% |
| 3 | phd | 5 | 3 | 40% |
| 4 | phd | 3 | 5 | 65% |

^aReactions run on 0.4 mmol scale and yields analyzed by calibrated GC using 1 eq. tetradecane as an internal standard.

VII. Additional Experiments and Observations

Figure S1 shows the effect of increasing the ligand:Cu ratio in the benzylic arylation reaction. As the ligand:Cu ratio increases from 0.5 to 6, formation of the desired product **B** increases and biaryl side-product **C** decreases. Only trace amounts of protodeboronation of the boronic ester is detected (**D**). The only other product that consumes >5% of the boronic ester is **E**, which is likely the result of arylation of in situ-generated bibenzyl. The amount of **E** is relatively constant once the ligand:Cu ratio exceeds 1.

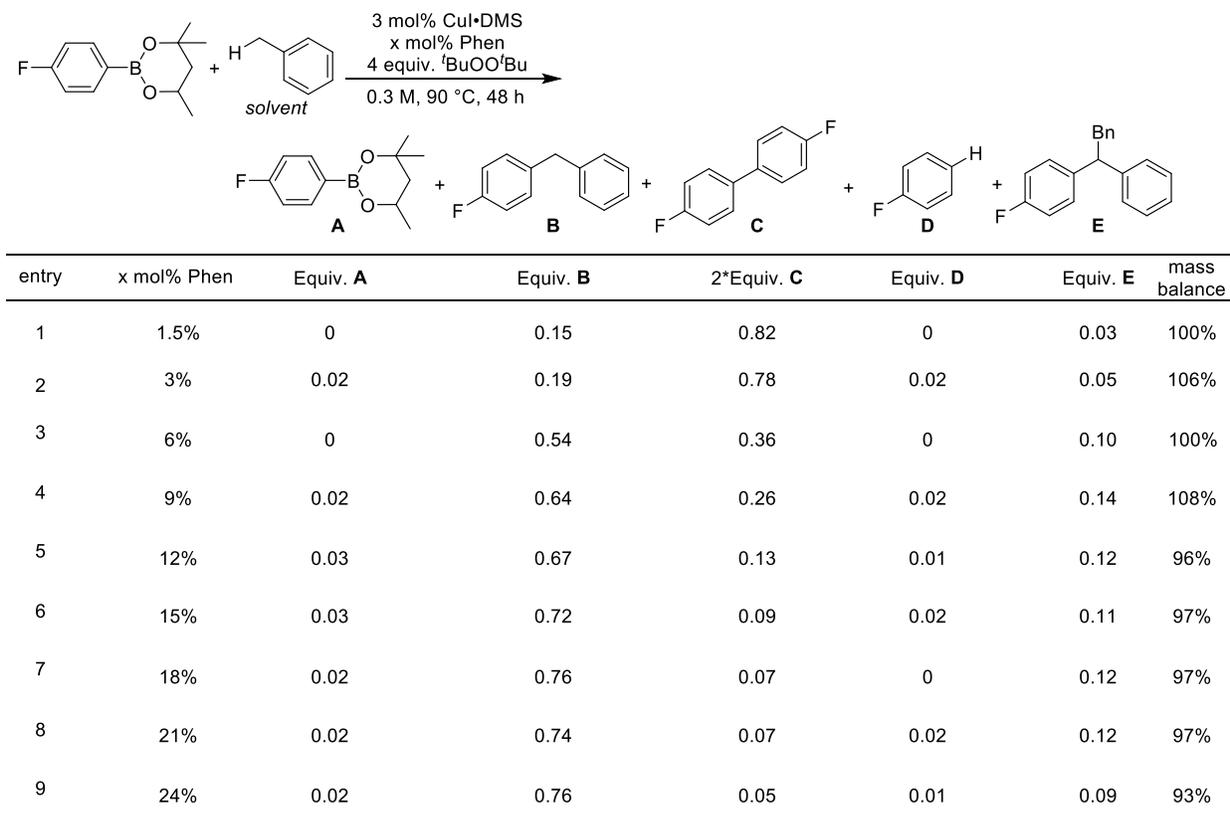


Figure S1: Product Distribution as a Function of the Ligand:Cu Ratio. ^aReactions run on 0.4 mmol scale and yields analyzed by ¹H NMR and ¹⁹F NMR with 1 eq. CH₂Br₂ and 1 eq. CF₃Ph as internal standards.

Figure S2 compares the distribution of ArBdiol- and ArBpin-derived products. The data show that more biaryl is generated with ArBpin than with ArBdiol. This outcome may arise from more-rapid transmetalation by ArBpin, resulting in a higher concentration of a Cu–Ar species that could undergo disproportionation to generate biaryl. Similar to the data in Figure S1, **E** is also the only major byproduct when using ArBpin as the nucleophile (only trace amount of protodeboronation to **D** is observed).

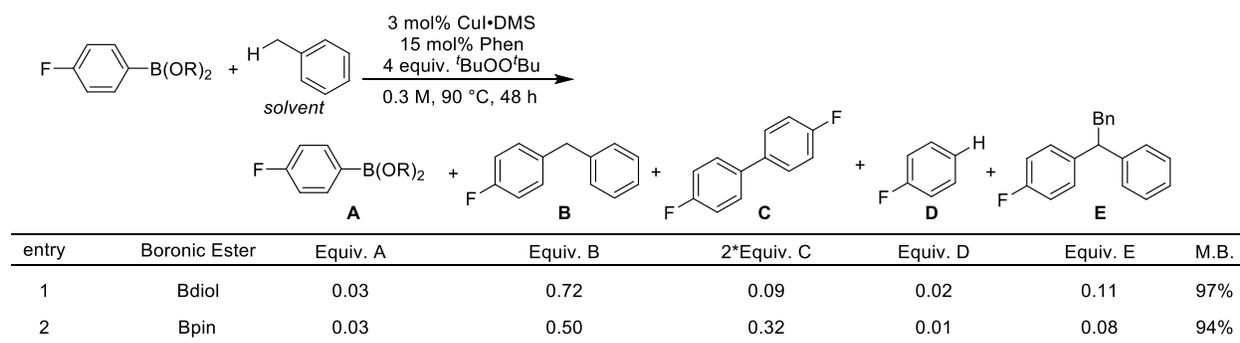


Figure S2: Distribution of Products for ArBdiol vs ArBpin. ^aReactions run on 0.4 mmol scale and yields analyzed by ¹H NMR and ¹⁹F NMR with 1 eq. CH₂Br₂ and 1 eq. CF₃Ph as internal standards. M. B. = mass balance.

Several competition experiments were carried out to probe the selectivity with respect to the arylboron nucleophile. The effect of the electronic property of the arylboronic ester showed a slight preference for the more-electron-rich aryl boronic ester nucleophile (Figure S3A). The effect of the diol fragment in the aryl boronic ester showed a slight preference for the Bpin derivative over the "Bdiol" derivative (i.e., the 4,4,6-trimethyl-1,3,2-dioxaborinane) (Figure S3B). Comparison of Bdiol vs. BF_3K shows exclusive selectivity for 4-F-PhBdiol over PhBF_3K (Figure S3C).

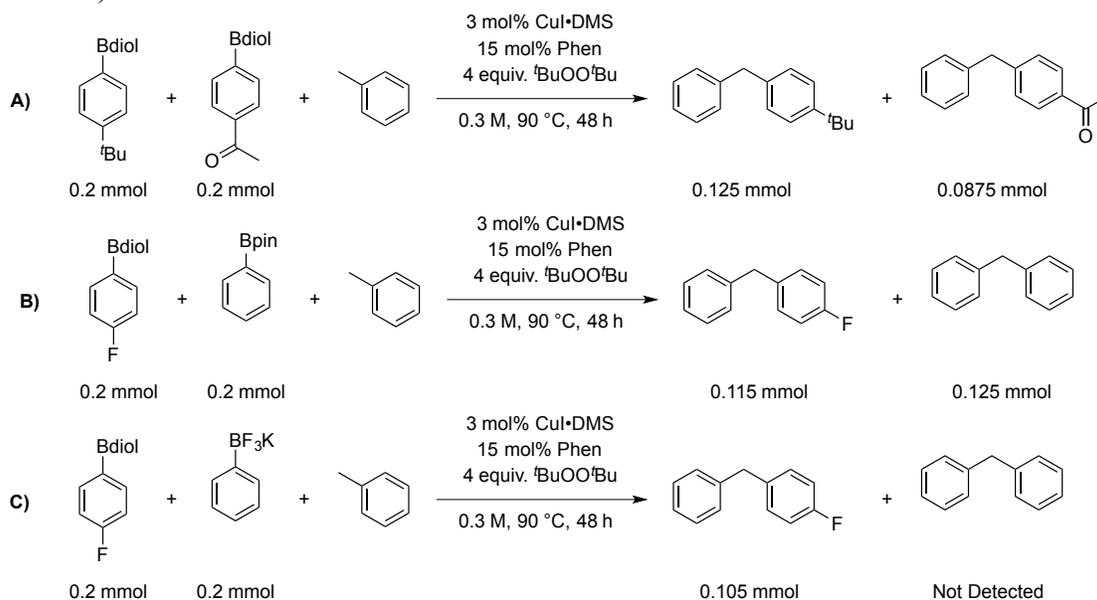


Figure S3: Competition Experiments Between Boron Nucleophiles. ^aReactions run on 0.4 mmol scale and yields analyzed by ¹H NMR and ¹⁹F NMR with 1 eq. CH_2Br_2 and 1 eq. CF_3Ph as internal standards.

Figure S4A depicts a competition reaction between toluene and ethyl benzene and shows that ethyl benzene undergoes preferential benzylic arylation over toluene in a ratio of 2.3 to 1. Figure S4B depicts an intramolecular competition reaction between the primary and tertiary C–H bonds of cumene. No observed oxidation of the tertiary C–H bond, while 0.33 equiv. of the diaryl methane of cumene was detected by ^1H NMR. Tertiary C–H bonds appear to be unreactive under the catalytic conditions (See Figure S7).

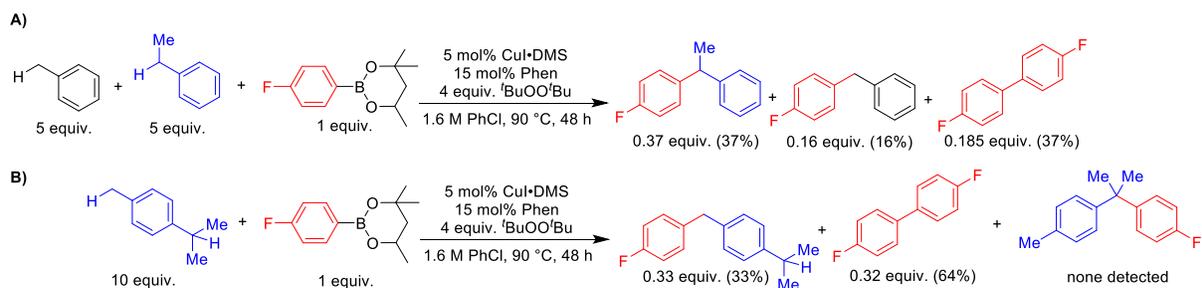


Figure S4: Selectivity Experiment for Primary vs Secondary and Primary vs Tertiary C–H Functionalization. ^aReactions run on 0.4 mmol scale and yields analyzed by ^1H NMR and ^{19}F NMR with 1 eq. CH_2Br_2 and 1 eq. CF_3Ph as internal standards.

In Figure S5 depicts experiments to assess the relative reactivity of methyl arene and diarylmethane C–H bonds. In reaction A, a control experiment is conducted with toluene. In reaction B, diphenylmethane undergoes 25% conversion under standard catalytic conditions, generating primarily 1,1,2,2-tetraphenylethane as the product (via homocoupling of the benzylic radical). In a competition experiment between toluene and diphenylmethane, under conditions reflecting typical reaction conditions, only 10% of diphenylmethane conversion is observed. These observations suggest that the diarylmethane products of the benzylic arylation reactions are not especially susceptible to overoxidation.

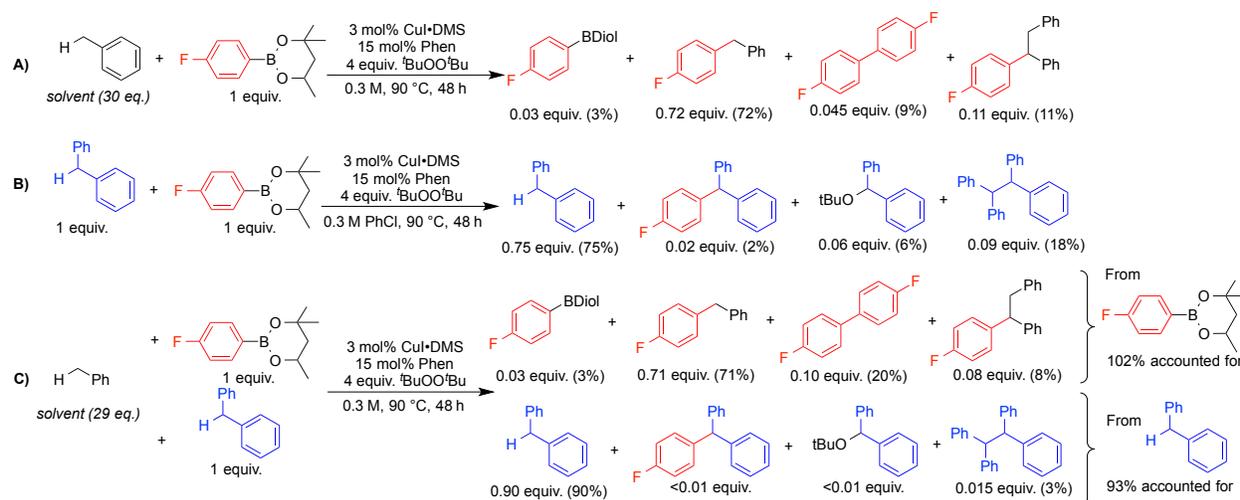


Figure S5: Selectivity Experiment for C–H Arylation of a Methyl Arene vs a Diarylmethane. ^aReactions run on 0.4 mmol scale and yields analyzed by ¹H NMR and ¹⁹F NMR with 1 eq. CH₂Br₂ and 1 eq. CF₃Ph as internal standards.

Figure S6 provides information on the relative reactivity of secondary and tertiary benzylic C–H bonds, using ethylbenzene and 1,1-diphenylpropane as the substrate. Even in the absence of ethylbenzene, only 1% conversion of the benzylic tertiary C–H bond is observed. When 9 equivalents of ethylbenzene is present (reflecting typical reaction conditions), no conversion of 1,1-diphenylpropane is detected, while ethylbenzene is converted into the corresponding diarylalkane in 57% yield.

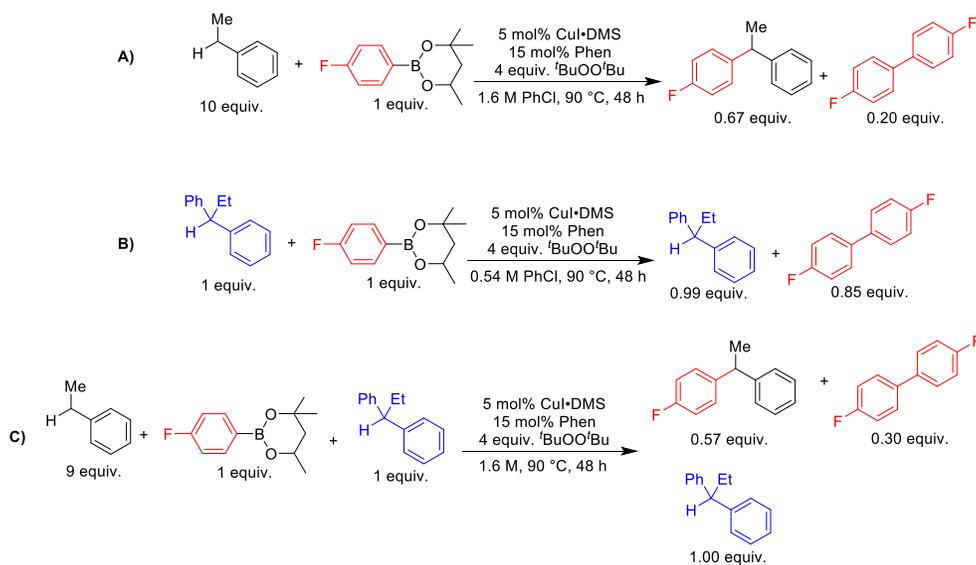
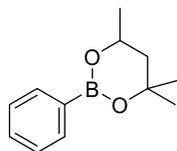


Figure S6: Comparative reactivity of ethylbenzene and 1,1-diphenylpropane. ^aReactions run on 0.4 mmol scale and yields analyzed by ¹H NMR and ¹⁹F NMR with 1 eq. CH₂Br₂ and 1 eq. CF₃Ph as internal standards.

VIII. Experimental Data for the ArBdiol Products (Compounds 1a-28a)



(1a) 2-Phenyl-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using Phenylboronic acid (40 mmol, 4.88 g).

Reaction duration: 16 h. Purification: Extraction and a SiO₂ plug, 90% pentane/Et₂O.

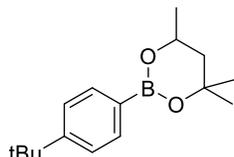
Yield: 95% (7.72 g), colorless oil.

Readily Purchasable (CAS): Yes (15961-35-0). As the BPin (CAS): Yes (24388-23-6)

Spectra Available in the Literature: Yes¹

¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, J = 6.6 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 4.36 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.88 (dd, J = 13.9, 3.0 Hz, 1H), 1.61 (dd, 1H), 1.39 (s, 3H), 1.38 (s, 3H), 1.36 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 133.73, 130.31, 127.43, 70.96, 64.96, 46.05, 31.30, 28.17, 23.23.



(2a) 2-(4-tert-Butylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-tert-Butylphenylboronic acid (5 mmol, 890 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 98% (1.27 g), white solid.

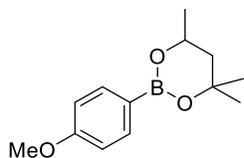
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (214360-66-4)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 4.33 (dq, J = 12.2, 6.2, 2.9 Hz, 1H), 1.85 (dd, J = 13.9, 2.9 Hz, 1H), 1.57 (dd, J = 13.9, 11.6 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H), 1.32 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 153.35, 133.60, 124.38, 70.78, 64.86, 46.09, 34.72, 31.31, 31.24, 28.12, 23.26.

HRMS (ESI) Calculated for C₁₆H₂₅BO₂ ([M+H]⁺): 260.2057, measured: 260.2053.



(3a) 2-(4-Methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Methoxyphenylboronic acid (7.5 mmol, 1.14 g).

Reaction duration: 4 h. Purification: Extraction.

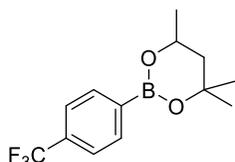
Yield: 94% (1.65 g), colorless oil.

Readily Purchasable (CAS): Yes (934558-31-3) As the BPin (CAS): Yes (171364-79-7)

Spectra Available in the Literature: Yes¹

¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.33 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 3.82 (s, 3H), 1.85 (dd, J = 13.8, 3.0 Hz, 1H), 1.58 (dd, J = 13.5, 11.7 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 161.49, 135.41, 113.00, 70.81, 64.86, 55.06, 46.08, 31.36, 28.18, 23.29.



(4a) 2-(4-Trifluoromethylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Trifluoromethylphenylboronic acid (2.5 mmol, 475 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 91% (622 mg), white solid.

Readily Purchasable (CAS): No (1214273-27-4) As the BPin (CAS): Yes (214360-65-3)

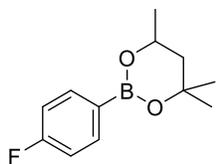
Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 4.37 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.89 (dd, J = 13.9, 2.9 Hz, 1H), 1.61 (dd, J = 13.9, 11.6 Hz, 1H), 1.39 (s, 3H), 1.38 (s, 3H), 1.36 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 133.98, 131.90 (q, J = 31.9 Hz), 124.35 (q, J = 272.2 Hz), 123.98 (q, J = 3.8 Hz), 71.38, 65.24, 45.96, 31.18, 28.13, 23.10.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.83.

HRMS (ESI) Calculated for C₁₃H₁₆BO₂F₃ ([M+H]⁺): 272.1305, measured: 272.1303.



(5a) 2-(4-Fluorophenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Fluorophenylboronic acid (7.5 mmol, 1.05 g).

Reaction duration: 16 h. Purification: Extraction and a SiO₂ plug, 90% pentane/Et₂O.

Yield: 80% (1.34 g), slightly yellow oil.

Readily Purchasable (CAS): Yes (1029653-69-7) As the BPin (CAS): Yes (214360-58-4)

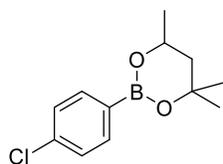
Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.80 (dd, J = 8.5, 6.4 Hz, 2H), 7.01 (t, J = 9.0 Hz, 2H), 4.34 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.87 (dd, J = 13.9, 3.0 Hz, 1H), 1.58 (dd, J = 14.1, 11.8 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 164.64 (d, J = 248.4 Hz), 135.85 (d, J = 8.0 Hz), 114.38 (d, J = 19.9 Hz), 71.06, 65.01, 45.99, 31.26, 28.14, 23.18.

¹⁹F NMR (377 MHz, CDCl₃) δ -110.55.

HRMS (ESI) Calculated for C₁₂H₁₆BFO₂ ([M+H]⁺): 222.1336, measured: 222.1336.



(6a) 2-(4-Chlorophenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Chlorophenylboronic acid (7.5 mmol, 1.17 g).

Reaction duration: 16 h. Purification: Extraction and a SiO₂ plug, 90% pentane/Et₂O.

Yield: 75% (1.34 g), yellow oil.

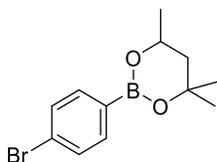
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (195062-61-4)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 4.34 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.87 (dd, J = 13.9, 2.9 Hz, 1H), 1.58 (dd, J = 13.9, 11.6 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 136.45, 135.18, 127.63, 71.16, 65.08, 45.97, 31.23, 28.15, 23.16.

HRMS (ESI) Calculated for C₁₂H₁₆BClO₂ ([M+H]⁺): 238.1041, measured: 238.1041.



(7a) 2-(4-Bromophenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Bromophenylboronic acid (2.5 mmol, 502 mg).

Reaction duration: 16 h. Purification: Extraction.

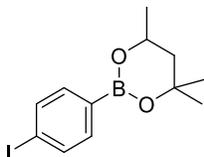
Yield: 96% (677 mg), colorless oil.

Readily Purchasable (CAS): Yes (1092060-78-0) As the BPin (CAS): Yes (68716-49-4)

Spectra Available in the Literature: Yes²

¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 4.33 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.87 (dd, J = 13.9, 2.9 Hz, 1H), 1.58 (dd, J = 13.9, 11.6 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 135.43, 130.57, 125.15, 71.18, 65.09, 45.96, 31.23, 28.14, 23.15.



(8a) 2-(4-Iodophenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Iodophenylboronic acid (2.5 mmol, 619.7 mg).

Reaction duration: 16 h. Purification: Extraction and a SiO₂ plug, 90% pentane/Et₂O.

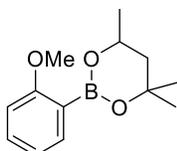
Yield: 90% (745 mg), thick off-white oil.

Readily Purchasable (CAS): Yes (1279115-53-5) As the BPin (CAS): Yes (73852-88-7)

Spectra Available in the Literature: Yes³

¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 4.33 (dq, J = 12.2, 6.2, 2.9 Hz, 1H), 1.86 (dd, J = 13.9, 2.8 Hz, 1H), 1.58 (dd, J = 13.9, 11.6 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.33 (d, J = 6.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 136.56, 135.48, 97.68, 71.18, 65.09, 45.95, 31.21, 28.14, 23.14.



(9a) 2-(2-Methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 2-Methoxyphenylboronic acid (2.5 mmol, 380 mg).

Reaction duration: 16 h. Purification: Extraction.

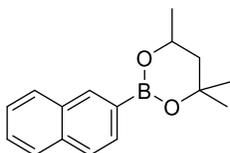
Yield: 95% (554 mg), white solid.

Readily Purchasable (CAS): Yes (934558-37-9) As the BPin (CAS): Yes (190788-60-4)

Spectra Available in the Literature: Yes¹

¹H NMR (500 MHz, CDCl₃) δ 7.60 (dd, J = 7.3, 1.9 Hz, 1H), 7.32 (ddd, J = 8.2, 7.3, 1.9 Hz, 1H), 6.92 (td, J = 7.3, 0.9 Hz, 1H), 6.83 (dd, J = 8.3, 0.9 Hz, 1H), 4.38 (ddh, J = 12.4, 6.2, 3.0 Hz, 1H), 3.81 (s, 3H), 1.86 (dd, J = 13.9, 3.0 Hz, 1H), 1.64 (dd, J = 13.8, 11.7 Hz, 1H), 1.39 (s, 3H), 1.38 (s, 3H), 1.35 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 163.50, 135.45, 131.14, 120.27, 110.90, 71.13, 65.18, 55.83, 45.96, 31.28, 28.17, 23.20.



(10a) 2-(2-Naphthyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using Naphthalene-2-boronic acid (2.5 mmol, 430 mg).

Reaction duration: 16 h. Purification: Extraction.

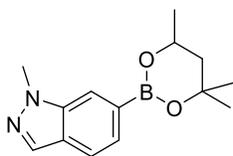
Yield: 98% (630 mg), viscous slightly yellow oil.

Readily Purchasable (CAS): Yes (1260068-92-5) As the BPin (CAS): Yes (256652-04-7)

Spectra Available in the Literature: Yes⁵

¹H NMR (500 MHz, CDCl₃) δ 8.35 (s, 1H), 7.89 (t, J = 7.4 Hz, 2H), 7.85 – 7.77 (m, 2H), 7.51 – 7.43 (m, 2H), 4.41 (dq, J = 12.2, 6.2, 2.9 Hz, 1H), 1.91 (dd, J = 13.9, 2.9 Hz, 1H), 1.65 (dd, J = 13.8, 11.6 Hz, 1H), 1.43 (s, 3H), 1.42 (s, 3H), 1.41 (d, J = 5.9 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 134.73, 134.72, 132.91, 130.06, 128.63, 127.61, 126.58, 126.34, 125.39, 71.14, 65.11, 46.09, 31.35, 28.24, 23.27.



(11a) 2-(6-Methylindazole)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 1-Methylindazole-6-boronic acid (2.5 mmol, 440 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 69% (445 mg), white solid.

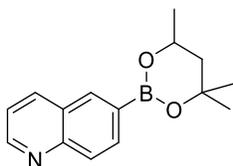
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (1256359-09-7)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, J = 1.0 Hz, 1H), 7.89 (d, J = 1.0 Hz, 1H), 7.68 (dd, J = 8.2, 1.0 Hz, 1H), 7.58 (dd, J = 8.1, 0.8 Hz, 1H), 4.40 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 4.12 (s, 3H), 1.91 (dd, J = 13.9, 2.9 Hz, 1H), 1.64 (dd, J = 13.7, 11.9 Hz, 1H), 1.41 (s, 3H), 1.40 (s, 3H), 1.39 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 139.89, 132.42, 125.41, 125.16, 119.75, 114.74, 71.25, 65.20, 46.08, 35.59, 31.34, 28.23, 23.27.

HRMS (ESI) Calculated for C₁₄H₁₉BN₂O₂ ([M+H]⁺): 258.1649, measured: 258.1651.



(12a) 2-(6-Quinoline)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using Quinoline-6-boronic acid (3 mmol, 519 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 64% (490 mg), colorless oil.

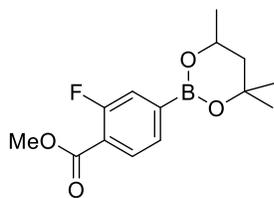
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (406463-06-7)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.93 (dd, J = 4.4, 1.7 Hz, 1H), 8.33 (d, J = 1.3 Hz, 1H), 8.21 (dd, J = 8.4, 1.6 Hz, 1H), 8.14 (dd, J = 8.5, 1.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.39 (dd, J = 8.2, 4.2 Hz, 1H), 4.43 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.93 (dd, J = 13.9, 2.9 Hz, 1H), 1.67 (dd, J = 13.9, 11.6 Hz, 1H), 1.45 (s, 3H), 1.43 (s, 3H), 1.42 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 150.84, 149.57, 136.69, 134.62, 133.92, 128.05, 127.66, 120.83, 71.37, 65.26, 46.05, 31.31, 28.24, 23.23.

HRMS (ESI) Calculated for C₁₅H₁₈BNO₂ ([M+H]⁺): 255.1540, measured: 255.1540.



(13a) 2-(3-Fluoro-4-Methoxycarbonylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 3-Fluoro-4-Methoxycarbonylphenyl boronic acid (3 mmol, 594 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 90% (758 mg), colorless oil.

Readily Purchasable (CAS): No (1214273-29-6) As the BPin (CAS): Yes (603122-52-7)

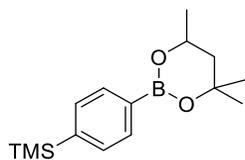
Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.89 (t, J = 7.4 Hz, 1H), 7.62 (dd, J = 7.6, 1.0 Hz, 1H), 7.55 (dd, J = 11.6, 1.0 Hz, 1H), 4.37 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 3.95 (s, 3H), 1.91 (dd, J = 14.0, 3.0 Hz, 1H), 1.69 – 1.57 (m, 1H), 1.40 (s, 3H), 1.39 (s, 3H), 1.37 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 165.25 (d, J = 3.6 Hz), 161.46 (d, J = 259.4 Hz), 130.96, 128.94 (d, J = 3.7 Hz), 121.69 (d, J = 20.6 Hz), 119.70 (d, J = 10.0 Hz), 71.62, 65.39, 52.26, 45.92, 31.14, 28.15, 23.06.

¹⁹F NMR (377 MHz, CDCl₃) δ -112.13.

HRMS (ESI) Calculated for C₁₄H₁₈BFO₄ ([M+H]⁺): 280.1391, measured: 280.1390.



(14a) 2-(4-Trimethylsilylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared per the general procedure in Section II using 4-Trimethylsilylphenylboronic acid (2.5 mmol, 485 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 96% (662 mg), white solid (becomes pink over time on the shelf).

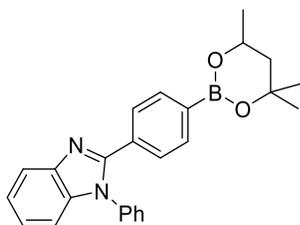
Readily Purchasable (CAS): No (N/A) As BPin (CAS): Yes (1186026-67-4)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 4.34 (dq, J = 12.3, 6.2, 3.0 Hz, 1H), 1.86 (dd, J = 13.8, 2.9 Hz, 1H), 1.58 (dd, J = 14.2, 11.6 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H), 0.26 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 142.79, 132.87, 132.36, 70.90, 64.94, 46.07, 31.28, 28.13, 23.23, -1.21.

HRMS (ESI) Calculated for C₁₅H₂₅BO₂Si ([M+H]⁺): 276.1826, measured: 276.1824.



(15a) 2-(4-(1-Phenyl-1H-benzimidazol-2-yl)phenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane:

Prepared according to the general procedure in Section II using 4-(1-Phenyl-1H-benzimidazol-2-yl)phenylboronic acid (2 mmol, 628 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 68% (808 mg), white solid.

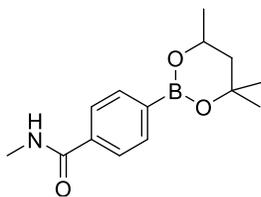
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): No (1146340-38-6)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.92 (dt, J = 8.0, 0.9 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.60 – 7.54 (m, 2H), 7.54 – 7.44 (m, 3H), 7.39 – 7.23 (m, 5H), 4.35 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.88 (dd, J = 13.9, 2.9 Hz, 1H), 1.60 (dd, J = 13.9, 11.6 Hz, 1H), 1.38 (s, 3H), 1.37 (s, 3H), 1.35 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.68, 143.06, 137.29, 137.11, 133.61, 131.45, 129.82, 128.47, 127.45, 123.29, 122.94, 119.86, 110.43, 71.21, 65.11, 45.99, 31.25, 28.19, 23.17.

HRMS (ESI) Calculated for C₂₅H₂₅BN₂O₂ ([M+H]⁺): 396.2118, measured: 396.2115.



(16a) 2-(4-(N-Methylaminocarbonyl)phenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-(N-Methylaminocarbonyl)phenyl boronic acid (2.5 mmol, 450 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 90% (587 mg), white solid.

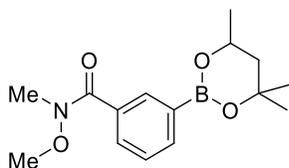
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (214360-57-3)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 6.08 (s, 1H), 4.28 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 2.95 (d, J = 4.8 Hz, 3H), 1.81 (dd, J = 13.9, 2.9 Hz, 1H), 1.56 – 1.48 (m, 1H), 1.31 (s, 3H), 1.30 (s, 3H), 1.28 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 168.41, 135.96, 133.97, 125.70, 71.30, 65.18, 46.00, 31.24, 28.19, 26.82, 23.16.

HRMS (ESI) Calculated for C₁₄H₂₀BNO₃ ([M+H]⁺): 261.1645, measured: 261.1647.



(17a) 2-(3-(N,O-Dimethylhydroxylaminocarbonyl)phenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 3-(N,O-Dimethylhydroxylaminocarbonyl)phenylboronic acid (3 mmol, 627 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 93% (809 mg), colorless oil.

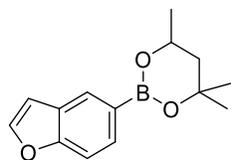
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (957061-17-5)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, J = 1.7 Hz, 1H), 7.90 (dd, J = 7.5, 1.5 Hz, 1H), 7.69 (dt, J = 7.8, 1.6 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 4.36 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 3.58 (s, 3H), 3.36 (s, 3H), 1.89 (dd, J = 13.9, 2.9 Hz, 1H), 1.60 (dd, J = 13.9, 11.6 Hz, 1H), 1.39 (s, 3H), 1.38 (s, 3H), 1.36 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.68, 135.89, 133.42, 133.32, 129.79, 127.03, 71.18, 65.10, 60.95, 46.02, 31.27, 28.18, 23.19.

HRMS (ESI) Calculated for C₁₅H₂₂BNO₄ ([M+H]⁺): 291.1751, measured: 291.1749.



(18a) 2-(5-Benzofuran)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using Benzofuran-5-boronic acid (2.5 mmol, 405 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: >99% (609 mg), slightly yellow oil.

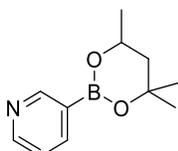
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (519054-55-8)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.11 (s, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.59 (d, J = 2.2 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 6.77 (d, J = 1.2 Hz, 1H), 4.38 (dq, J = 12.4, 6.2, 2.9 Hz, 1H), 1.88 (dd, J = 13.8, 2.9 Hz, 1H), 1.62 (dd, J = 13.8, 11.6 Hz, 1H), 1.40 (s, 3H), 1.39 (s, 3H), 1.38 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.71, 144.56, 129.93, 127.41, 126.91, 110.46, 106.74, 71.00, 65.01, 46.08, 31.38, 28.22, 23.30.

HRMS (ESI) Calculated for C₁₄H₁₇BO₃ ([M+H]⁺): 244.1380, measured: 244.1379.



(19a) 2-(3-Pyridyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using Pyridine-3-boronic acid (2 mmol, 246 mg) with methanol as the solvent instead of dichloromethane.

Reaction duration: 16 h. Purification: Extraction and a filtration over a frit with 90% pentane/Et₂O (collected the filtrate).

Yield: 50% (205 mg), yellow oil.

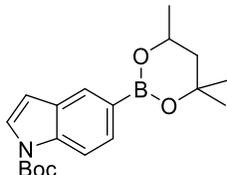
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (329214-79-1)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.92 (t, J = 1.3 Hz, 1H), 8.60 (dd, J = 4.9, 1.9 Hz, 1H), 8.03 (dt, J = 7.5, 1.9 Hz, 1H), 7.22 (ddd, J = 7.5, 4.9, 1.0 Hz, 1H), 4.35 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.88 (dd, J = 14.0, 3.0 Hz, 1H), 1.60 (dd, J = 14.0, 11.6 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 154.86, 151.12, 141.36, 122.83, 71.41, 65.24, 46.02, 31.19, 28.15, 23.12.

HRMS (ESI) Calculated for C₁₁H₁₆BNO₂ ([M+H]⁺): 205.1383, measured: 205.1385.



(20a) 2-(5-H-Indole)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 1H-Indole-5-boronic acid (1 mmol, 161 mg).

Reaction duration: 16 h. Purification: Extraction and a SiO₂ plug, 90% pentane/Et₂O.

Yield: 82%

Boc Protection⁴: The H-IndoleBdiol (0.82 mmol, 200 mg, 1 equiv.) was stirred with Boc₂O (1.97 mmol, 429 mg, 2.4 equiv.), Triethylamine (0.98 mmol, 137 μL, 1.2 equiv.), and 4-Dimethylaminopyridine (0.082 mmol, 10 mg, 0.1 equiv.) in dichloromethane (1 mL, 0.8 M).

Reaction duration: 24 h. Purification: Acidic extraction and a SiO₂ plug, 90% pentane/Et₂O.

Overall Yield: 63% (82% and 77% respectively, yielding 216 mg of product), white solid.

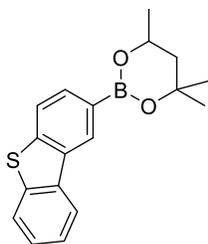
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (777061-36-6)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 1.0 Hz, 1H), 7.77 (dd, J = 8.4, 1.2 Hz, 1H), 7.55 (d, J = 3.8 Hz, 1H), 6.57 (d, J = 3.8 Hz, 1H), 4.37 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.88 (dd, J = 13.9, 2.9 Hz, 1H), 1.67 (s, 9H), 1.62 (dd, J = 13.9, 11.6 Hz, 1H), 1.40 (s, 3H), 1.39 (s, 3H), 1.37 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 149.84, 136.83, 130.11, 129.76, 127.05, 125.53, 114.15, 107.70, 83.51, 70.94, 64.96, 46.10, 31.39, 28.24, 28.23, 23.31.

HRMS (ESI) Calculated for C₁₉H₂₆BNO₄ ([M+H]⁺): 343.2064, measured: 343.2060.



(21a) 2-(2-Dibenzothiophene)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using Dibenzothiophene-2-boronic acid (3 mmol, 684 mg).

Reaction duration: 16 h. Purification: Extraction.

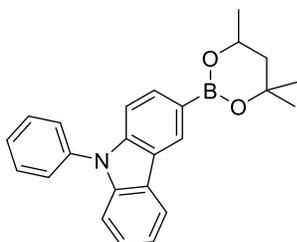
Yield: 85% (792 mg), white solid.

Readily Purchasable (CAS): No (N/A) As the BPin (CAS): No (890042-21-4)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.64 (d, J = 7.6 Hz, 1H), 8.39 – 8.28 (m, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.87 (td, J = 7.2, 2.3 Hz, 2H), 7.48 (tt, J = 4.6, 1.8 Hz, 2H), 4.44 (dq, J = 12.3, 6.1, 3.2 Hz, 1H), 1.94 (dd, J = 13.9, 2.9 Hz, 1H), 1.68 (dd, J = 13.8, 11.7 Hz, 1H), 1.49 – 1.41 (m, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 141.80, 139.17, 135.87, 134.95, 131.95, 127.21, 126.43, 124.29, 122.70, 121.80, 71.22, 65.17, 46.12, 31.38, 28.26, 23.31.



(22a) 2-(3-(9-Phenyl-9H-carbazole))-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 9-Phenyl-9H-carbazole-3-boronic acid (4 mmol, 1.15 g).

Reaction duration: 16 h. Purification: Extraction.

Yield: 93% (1.366 g), white solid.

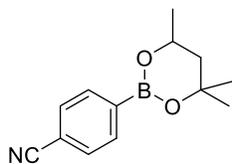
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (1126522-69-7)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.55 (t, J = 0.9 Hz, 1H), 8.13 (dt, J = 7.6, 1.0 Hz, 1H), 7.80 (dd, J = 8.3, 1.1 Hz, 1H), 7.56 – 7.47 (m, 4H), 7.41 – 7.36 (m, 1H), 7.34 – 7.26 (m, 3H), 7.21 (ddd, J = 8.0, 5.5, 2.6 Hz, 1H), 4.34 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.83 (dd, J = 13.8, 2.9 Hz, 1H), 1.58 (dd, J = 13.8, 11.6 Hz, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 142.61, 140.96, 137.74, 131.62, 129.82, 127.38, 127.12, 126.50, 125.60, 123.80, 122.94, 120.49, 119.98, 109.66, 108.81, 70.96, 65.01, 46.20, 31.46, 28.27, 23.39.

HRMS (ESI) Calculated for C₂₄H₂₄BNO₂ ([M+H]⁺): 369.2009, measured: 369.2007.



(23a) 2-(4-Cyanophenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Cyanophenylboronic acid (2.5 mmol, 367 mg).

Reaction duration: 16 h. Purification: Extraction.

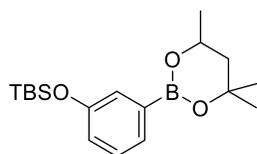
Yield: 87% (498 mg), white solid.

Readily Purchasable (CAS): Yes (1092060-81-5) As the BPin (CAS): (171364-82-2)

Spectra Available in the Literature: Yes²

¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 6.3 Hz, 2H), 4.36 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.89 (dd, J = 14.0, 2.9 Hz, 1H), 1.60 (dd, J = 14.0, 11.7 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.35 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 134.17, 130.91, 119.29, 113.55, 71.62, 65.40, 45.93, 31.16, 28.16, 23.08.



(24a) 2-(3-*tert*-Butyldimethylsilyloxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 3-(*tert*-Butyldimethylsilyloxy)phenylboronic acid (2.5 mmol, 630 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 87% (725 mg), colorless oil.

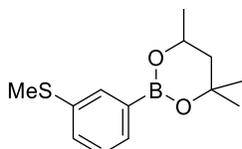
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (902120-00-7)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.40 (dd, J = 7.3, 1.1 Hz, 1H), 7.27 (d, J = 2.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 6.87 (ddd, J = 7.9, 2.7, 1.2 Hz, 1H), 4.33 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 1.85 (dd, J = 13.9, 3.0 Hz, 1H), 1.58 (dd, J = 14.0, 11.8 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.34 (d, J = 6.2 Hz, 3H), 0.99 (s, 9H), 0.20 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 154.99, 128.49, 126.64, 125.09, 121.99, 70.92, 64.93, 46.01, 31.26, 28.15, 25.75, 23.19, 18.21, -4.16, -4.38, -4.61.

HRMS (ESI) Calculated for C₁₈H₃₁BO₃Si ([M+H]⁺): 334.2245, measured: 334.2244.



(25a) 2-(3-Methylthiophenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 3-Methylthiophenylboronic acid (2.5 mmol, 420 mg).

Reaction duration: 16 h. Purification: Extraction and a SiO₂ plug, 90% pentane/Et₂O.

Yield: 94% (587 mg), off-white solid.

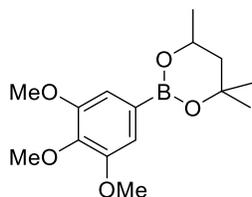
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (710348-63-3)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.73 (dd, J = 2.0, 1.0 Hz, 1H), 7.59 (dt, J = 7.3, 1.3 Hz, 1H), 7.32 (ddd, J = 7.8, 2.2, 1.4 Hz, 1H), 7.26 (dd, J = 8.6, 6.4 Hz, 1H), 4.34 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 2.50 (s, 3H), 1.87 (dd, J = 13.9, 2.9 Hz, 1H), 1.58 (dd, J = 14.1, 11.4 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.35 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 137.16, 132.37, 130.66, 128.88, 127.98, 71.11, 65.07, 46.02, 31.26, 28.16, 23.20, 16.18.

HRMS (ESI) Calculated for C₁₃H₁₉BO₂S ([M+H]⁺): 250.1308, measured: 250.1310.



(26a) 2-(3,4,5-Trimethoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 3,4,5-trimethoxyphenylboronic acid (1.5 mmol, 318 mg).

Reaction duration: 16 h. Purification: Extraction.

Yield: 76% (337 mg), white solid.

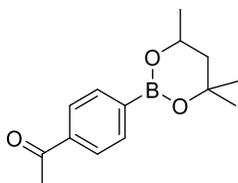
Readily Purchasable (CAS): No (N/A) As the BPin (CAS): Yes (214360-67-5)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.04 (s, 2H), 4.34 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 3.90 (s, 6H), 3.85 (s, 3H), 1.86 (dd, J = 13.9, 2.9 Hz, 1H), 1.57 (dd, J = 13.9, 11.6 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H), 1.35 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.70, 140.17, 110.32, 71.10, 65.08, 60.75, 56.07, 46.04, 31.27, 28.14, 23.23.

HRMS (ESI) Calculated for C₁₅H₂₃BO₅ ([M+H]⁺): 294.1748, measured: 294.1747.



(27a) 2-(4-Acetylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Acetylphenylboronic acid (2.5 mmol, 408 mg).

Reaction duration: 16 h. Purification: Extraction and a SiO₂ plug, 90% pentane/Et₂O.

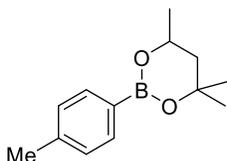
Yield: 95% (587 mg), colorless oil.

Readily Purchasable (CAS): Yes (934558-34-6) As the BPin (CAS): Yes (171364-81-1)

Spectra Available in the Literature: Yes⁵

¹H NMR (500 MHz, CDCl₃) δ 7.92 – 7.87 (m, 4H), 4.36 (dq, J = 12.3, 6.2, 2.9 Hz, 1H), 2.60 (s, 3H), 1.89 (dd, J = 14.0, 2.9 Hz, 1H), 1.60 (dd, J = 13.7, 11.8 Hz, 1H), 1.38 (s, 3H), 1.37 (s, 3H), 1.36 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 198.70, 138.33, 133.93, 127.11, 71.38, 65.24, 45.99, 31.23, 28.19, 26.77, 23.15.



(28a) 2-(4-Methylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane: Prepared according to the general procedure in Section II using 4-Methylphenylboronic acid (7.5 mmol, 1.02 g).

Reaction duration: 4 h. Purification: Extraction.

Yield: 83% (1.36 g), colorless oil (with some suspended white solid in the oil).

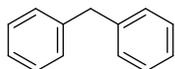
Readily Purchasable (CAS): Yes (1092060-77-9) As BPin (CAS): Yes (195062-57-8)

Spectra Available in the Literature: Yes²

¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, J = 7.6 Hz, 2H), 7.16 (d, J = 7.5 Hz, 2H), 4.34 (dq, J = 12.4, 6.2, 2.9 Hz, 1H), 2.36 (s, 3H), 1.86 (dd, J = 13.8, 2.9 Hz, 1H), 1.59 (dd, J = 14.3, 12.2 Hz, 1H), 1.38 (s, 3H), 1.37 (s, 3H), 1.35 (d, J = 6.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 140.23, 133.82, 128.26, 70.85, 64.89, 46.09, 31.35, 28.19, 23.28, 21.67.

IX. Experimental Data for 1,1-Diarylalkane Products (Compounds 1-43)



(1) Diphenylmethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

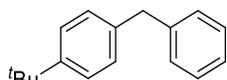
Yield: 78% (70%, 58.8 mg), colorless oil.

Readily Purchasable (CAS): Yes (101-81-5)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.28 (m, 4H), 7.25 – 7.20 (m, 6H), 4.02 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 141.12, 128.94, 128.46, 126.07, 41.95.



(2) 4-tert-Butyldiphenylmethane: Prepared from **2a** (0.5 mmol, 130.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

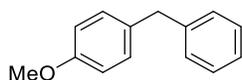
Yield: 76% (64%, 71.7 mg), colorless oil.

Readily Purchasable (CAS): No (16251-99-3)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.28 (m, 4H), 7.25 – 7.19 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 3.98 (s, 2H), 1.33 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 148.82, 141.27, 138.07, 128.96, 128.50, 128.42, 125.99, 125.34, 41.44, 34.37, 31.40.



(3) 4-Methoxydiphenylmethane: Prepared from **3a** (0.5 mmol, 117.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 80%→100%, extraction with 90% pentane/Et₂O.

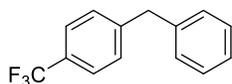
Yield: 70% (61%, 60.5 mg), cloudy oil.

Readily Purchasable (CAS): Yes (834-14-0)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 7.12 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.94 (s, 2H), 3.80 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.97, 141.60, 133.26, 129.88, 128.83, 128.44, 125.99, 113.88, 55.27, 41.05.



(4) 4-Trifluoromethyldiphenylmethane: Prepared from **13a** (0.5 mmol, 136.0 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

Yield: 63% (56%, 66.1 mg), off-white solid.

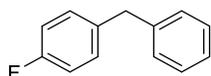
Readily Purchasable (CAS): Yes (34239-04-8)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, J = 8.0 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.24 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 7.1 Hz, 2H), 4.04 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 145.20 (q, J = 1.6 Hz), 143.25, 139.98, 129.19, 128.94, 128.67, 128.48 (q, J = 32.4 Hz), 126.47, 125.40 (q, J = 3.8 Hz), 41.73.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.37.



(5) 4-Fluorodiphenylmethane: Prepared from **5a** (0.5 mmol, 111.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 85%→100%, extraction with 90% pentane/Et₂O.

Yield: 70% (54%, 50.2 mg), slightly yellow oil.

OR

(5') Prepared from **1a** (0.5 mmol, 102.1 mg) and 4-fluorotoluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

Yield: 70%, slightly yellow oil. The product was obtained from the column as a mixture with <10% biaryl.

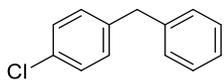
Readily Purchasable (CAS): Yes (587-79-1)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.20 (t, J = 7.5 Hz, 2H), 7.14 – 7.10 (m, 1H), 7.10 – 7.02 (m, 4H), 6.88 (t, J = 8.7 Hz, 2H), 3.86 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 161.44 (d, J = 243.9 Hz), 140.96, 136.79 (d, J = 3.2 Hz), 130.30 (d, J = 7.9 Hz), 128.85, 128.56, 126.23, 115.23 (d, J = 21.2 Hz), 41.11.

¹⁹F NMR (377 MHz, CDCl₃) δ -117.44.



(6) 4-Chlorodiphenylmethane: Prepared from **6a** (0.5 mmol, 119.2 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

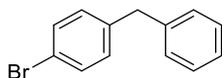
Yield: 65%, light yellow oil. The product was obtained from the column as a mixture with 12% bibenzyl.

Readily Purchasable (CAS): Yes (831-81-2)

Spectra Available in the Literature: Yes⁷

¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, J = 7.5 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.17 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 3.96 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 140.54, 139.57, 131.88, 130.24, 128.85, 128.56, 128.55, 126.28, 41.24.



(7) 4-Bromodiphenylmethane: Prepared from **7a** (0.5 mmol, 141.5 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89% → 100%, extraction with 90% pentane/Et₂O.

Yield: 64%, off-white oil. The product was obtained from the column as a mixture with ~20% bibenzyl.

OR

(7¹) Prepared from **1a** (0.5 mmol, 102.1 mg) and 4-bromotoluene (0.3 M, 1.6 mL) per Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

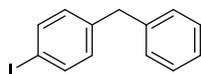
Yield: 61% (55%, 67.7 mg), off-white oil.

Readily Purchasable (CAS): Yes (2116-36-1)

Spectra Available in the Literature: Yes⁷

¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 8.4 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.16 (d, J = 7.0 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 3.94 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 140.43, 140.08, 131.50, 130.65, 128.84, 128.56, 126.29, 119.92, 41.29.



(8) 4-Iododiphenylmethane: Prepared from **8a** (0.5 mmol, 165 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

Yield: 67% (54%, 79.3 mg), colorless oil (decomposes to pink compound over time on bench).

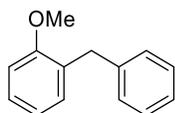
Readily Purchasable (CAS): Yes (35444-94-1)

Spectra Available in the Literature: Yes⁸ (Authors are missing some peaks)

¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.16 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 7.8 Hz, 2H), 3.92 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 140.78, 140.38, 137.48, 131.00, 128.85, 128.56, 126.29, 91.28, 41.40.

HRMS (ESI) Calculated for C₁₃H₁₁I ([M+H]⁺): 293.9900, measured: 293.9892.



(9) 2-Methoxydiphenylmethane: Prepared from **18a** (0.5 mmol, 117.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 70%→100%, extraction with 90% pentane/Et₂O.

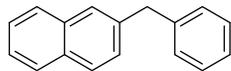
Yield: 46% (39%, 38.2 mg), yellow oil.

Readily Purchasable (CAS): No (883-90-9)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.24 (m, 2H), 7.24 – 7.15 (m, 4H), 7.09 – 7.05 (m, 1H), 6.91 – 6.84 (m, 2H), 3.98 (s, 2H), 3.82 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.30, 140.99, 130.28, 129.63, 128.93, 128.22, 127.37, 125.73, 120.43, 110.36, 55.32, 35.83.



(10) 2-Benzyl-naphthalene: Prepared from **19a** (0.5 mmol, 127.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

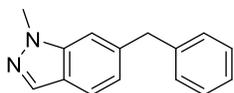
Yield: 69% (61%, 66.6 mg), colorless oil.

Readily Purchasable (CAS): No (613-59-2)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.85 – 7.76 (m, 3H), 7.67 (s, 1H), 7.46 (pd, J = 6.9, 1.5 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.29 – 7.22 (m, 3H), 4.18 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 140.99, 138.61, 133.62, 132.09, 129.04, 128.51, 128.09, 127.65, 127.63, 127.56, 127.11, 126.16, 125.99, 125.36, 42.13.



(11) N-Methyl-6-benzylindazole: Prepared from **9a** (0.5 mmol, 129.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10%→90%. The product was obtained with <10% of the over-benzylated product (analogous to **E** in Figure S1). Reverse-phase column (MeOH/H₂O with 0.1% TFA 89%→100%) was used on that sample to get a pure sample for characterization (with higher yield than the previous method).

Yield: 52% (46%, 52.1 mg), white solid.

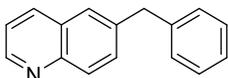
Readily Purchasable (CAS): No (N/A)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.92 (s, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 7.18 (s, 1H), 7.01 (d, J = 8.3 Hz, 1H), 4.14 (s, 2H), 4.03 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 140.93, 140.38, 139.74, 132.55, 128.94, 128.55, 126.24, 122.59, 122.47, 120.95, 108.55, 42.39, 35.48.

HRMS (ESI) Calculated for C₁₅H₁₄N₂ ([M+H]⁺): 223.1230, measured: 223.1229.



(12) 6-Benzylquinoline: Prepared from **12a** (0.5 mmol, 128 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10%→90%. The product was obtained with 13% of the over-benzylated product (analogous to **E** in Figure S1). Reverse-phase column (MeOH/H₂O with 0.1% TFA 89%→100%) was used on that sample to get a pure sample for characterization.

Yield: 39% (31%, 33.8 mg), colorless oil.

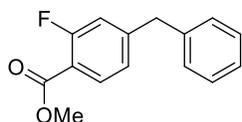
Readily Purchasable (CAS): No (54884-99-0)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.79 (dd, J = 4.2, 1.7 Hz, 1H), 8.00 (dd, J = 8.3, 0.9 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.29 (dd, J = 8.3, 4.2 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.12 (m, 3H), 4.10 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 149.90, 147.22, 140.43, 139.58, 135.70, 131.27, 129.54, 129.05, 128.63, 126.79, 126.38, 121.18, 41.90.

HRMS (ESI) Calculated for C₁₆H₁₃N ([M+H]⁺): 220.1121, measured: 220.1119.



(13) 3-Fluoro-4-methoxycarbonyldiphenylmethane : Prepared from **13a** (0.5 mmol, 140 mg) and toluene (0.3 M, 1.6 mL) according to Section III, except using 20 mol% Phen.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10%→90%. The product was obtained with <10% of the over-benzylated product. Reverse-phase column (MeOH/H₂O with 0.1% TFA 89%→100%) was used on that sample to get a pure sample for characterization.

Yield: 50% (45%, 54.7 mg), colorless oil.

Readily Purchasable (CAS): No (N/A)

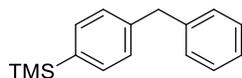
Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.78 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.14 (m, 1H), 7.09 (d, *J* = 6.9 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 11.8 Hz, 1H), 3.93 (s, 2H), 3.83 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 164.87 (d, *J* = 3.9 Hz), 163.08, 161.01, 149.04 (d, *J* = 8.4 Hz), 139.22, 132.21 (d, *J* = 1.4 Hz), 128.86 (d, *J* = 28.6 Hz), 126.67, 124.51 (d, *J* = 3.4 Hz), 117.25 (d, *J* = 22.6 Hz), 116.33 (d, *J* = 10.0 Hz), 52.23, 41.63 (d, *J* = 1.5 Hz).

¹⁹F NMR (377 MHz, CDCl₃) δ -109.62.

HRMS (ESI) Calculated for C₁₅H₁₃FO₂ ([M+H]⁺): 245.0972, measured: 245.0971.



(14) 4-Trimethylsilyldiphenylmethane: Prepared from **20a** (0.5 mmol, 138.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

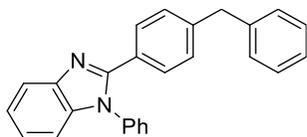
Yield: 71% (59%, 70.8 mg), colorless oil.

Readily Purchasable (CAS): No (17964-29-3)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 5H), 4.00 (s, 2H), 0.27 (d, *J* = 1.0 Hz, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 141.73, 140.96, 137.72, 133.54, 128.97, 128.46, 128.32, 126.08, 41.94, -1.06.



(15) 4-(1-Phenyl-1H-benzimidazol-2-yl)diphenylmethane : Prepared from **15a** (0.5 mmol, 198 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10%→90%. The product was obtained with <10% of the over-benzylated product. Reverse-phase column (MeOH/H₂O with 0.1% TFA 89%→100%) was used on that sample to get a pure sample for characterization.

Yield: 52% (46%, 82.1 mg), white solid.

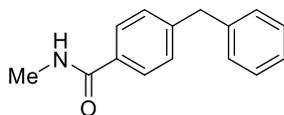
Readily Purchasable (CAS): No (N/A)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.36 (m, 5H), 7.26 – 7.10 (m, 8H), 7.08 (d, *J* = 6.7 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 152.34, 143.00, 142.64, 140.38, 137.30, 137.10, 129.87, 129.51, 129.00, 128.91, 128.57, 128.51, 127.48, 126.24, 123.22, 122.93, 119.75, 110.40, 41.68.

HRMS (ESI) Calculated for C₂₆H₂₀N₂ ([M+H]⁺): 361.1699, measured: 361.1694.



(16) 4-(N-Methylaminocarbonyl)diphenylmethane : Prepared from **16a** (0.5 mmol, 131 mg) and toluene (0.3 M, 1.6 mL) according to Section III, except using 27 mol% Phen.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10%→90%. The product was obtained with <10% of the over-benzylated product. Reverse-phase column (MeOH/H₂O with 0.1% TFA 89%→100%) was used on that sample to get a pure sample for characterization.

Yield: 46% (40%, 45.2 mg), white solid.

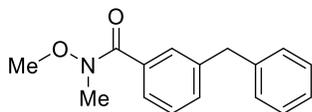
Readily Purchasable (CAS): No (N/A)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.12 (m, 5H), 7.10 (d, *J* = 6.9 Hz, 2H), 3.94 (s, 2H), 2.93 (d, *J* = 4.8 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 168.09, 144.77, 140.30, 132.51, 129.10, 128.93, 128.59, 127.05, 126.34, 41.75, 26.82.

HRMS (ESI) Calculated for C₁₅H₁₅NO ([M+H]⁺): 226.1226, measured: 226.1224.



(17) 3-(N,O-Dimethylhydroxylaminocarbonyl)diphenylmethane : Prepared from **17a** (0.5 mmol, 146 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10%→90%. The product was obtained with <10% of the over-benzylated product. Reverse-phase column (MeOH/H₂O with 0.1% TFA 89%→100%) was used on that sample to get a pure sample for characterization.

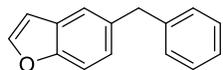
Yield: 43% (39%, 49.7 mg), white solid.

Readily Purchasable (CAS): No (422550-69-4)

Spectra Available in the Literature: Yes⁹

¹H NMR (500 MHz, CDCl₃) δ 7.42 (dt, *J* = 4.0, 1.8 Hz, 2H), 7.27 – 7.17 (m, 4H), 7.15 – 7.07 (m, 3H), 3.94 (s, 2H), 3.43 (s, 3H), 3.25 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.09, 141.03, 140.60, 134.29, 131.13, 128.97, 128.63, 128.53, 128.17, 126.24, 125.90, 60.99, 41.76.



(18) 5-Benzylbenzofuran: Prepared from **12a** (0.5 mmol, 122.0 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

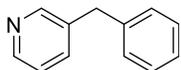
Yield: 50% (46%, 47.8 mg), colorless oil.

Readily Purchasable (CAS): No (939050-19-8)

Spectra Available in the Literature: Yes¹⁰

¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 1.7 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.24 – 7.20 (m, 3H), 7.14 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.70 (dd, *J* = 2.2, 1.0 Hz, 1H), 4.08 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 153.66, 145.15, 141.63, 135.62, 128.87, 128.44, 127.59, 126.02, 125.42, 121.10, 111.17, 106.45, 41.78.



(19) 3-Benzylpyridine: Prepared from **11a** (0.5 mmol, 102.5 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

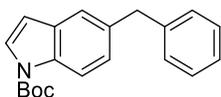
Yield: 41%, light yellow oil. Product was obtained from the column with <10% impurity of arylated bibenzyl byproduct.

Readily Purchasable (CAS): Yes (620-95-1)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 8.51 (s, 1H), 8.46 (d, J = 4.7 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.23 – 7.16 (m, 4H), 3.98 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 150.17, 147.65, 139.78, 136.45, 136.28, 128.84, 128.66, 126.47, 123.41, 39.04.



(20) N-Boc-5-benzylindole: Prepared from **10a** (0.5 mmol, 171.6 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 75%→100%, extraction with 90% pentane/Et₂O.

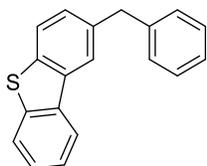
Yield: 40% (34%, 52.4 mg), slightly yellow oil.

Readily Purchasable (CAS): No (2031240-78-3)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 3.7 Hz, 1H), 7.37 (d, J = 1.6 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.23 – 7.19 (m, 3H), 7.16 (dd, J = 8.5, 1.7 Hz, 1H), 6.50 (d, J = 3.9 Hz, 1H), 4.08 (s, 2H), 1.67 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 149.78, 141.72, 135.47, 130.84, 128.87, 128.40, 126.08, 125.95, 125.45, 120.96, 115.04, 107.17, 83.53, 41.79, 29.70, 28.19.



(21) 4-Benzylidibenzothiophene: Prepared from **21a** (0.5 mmol, 155 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10%→90%. The product was obtained with <10% of the over-benzylated product. Reverse-phase column (MeOH/H₂O with 0.1% TFA 89%→100%) was used on that sample to get a pure sample for characterization.

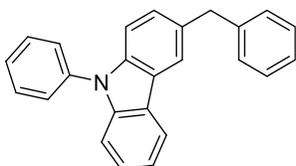
Yield: 57% (50%, 69.0 mg), colorless oil.

Readily Purchasable (CAS): No (98882-23-6)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.06 – 8.01 (m, 1H), 7.91 (d, *J* = 0.8 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.27 – 7.20 (m, 3H), 7.19 – 7.11 (m, 3H), 4.10 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 141.20, 139.83, 137.48, 137.22, 135.83, 135.42, 128.93, 128.55, 128.08, 126.63, 126.20, 124.24, 122.85, 122.75, 121.82, 121.58, 41.92.



(22) 3-(9-Phenyl-9H-carbazole)diphenylmethane : Prepared from **22a** (0.5 mmol, 184.5 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10%→90%. The product was obtained with <10% of the over-benzylated product. Reverse-phase column (MeOH/H₂O with 0.1% TFA 89%→100%) was used on that sample to get a pure sample for characterization.

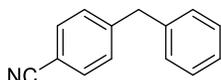
Yield: 47% (40%, 66.3 mg), white solid.

Readily Purchasable (CAS): No (857503-81-2)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.88 (s, 1H), 7.56 – 7.43 (m, 4H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.33 – 7.09 (m, 10H), 4.11 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 142.15, 141.18, 139.62, 137.88, 132.79, 129.89, 128.96, 128.52, 127.37, 127.29, 127.07, 126.03, 125.93, 123.62, 123.32, 120.49, 120.37, 119.86, 109.82, 109.83, 42.03.



(23) 4-Cyanodiphenylmethane: Prepared from **14a** (0.5 mmol, 114.6 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

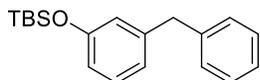
Yield: 54%, colorless oil. The product was obtained from the column as a mixture with <10% biaryl.

Readily Purchasable (CAS): No (23450-31-9)

Spectra Available in the Literature: Yes⁷

¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, J = 8.3 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 7.16 (d, J = 8.1 Hz, 2H), 4.04 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 146.72, 139.31, 132.29, 129.62, 128.94, 128.75, 126.66, 118.98, 110.03, 41.96.



(24) 3-tert-Butyldimethylsilyloxydiphenylmethane: Prepared from **15a** (0.5 mmol, 167.1 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

Yield: 73% (63%, 93.9 mg), colorless oil.

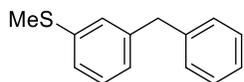
Readily Purchasable (CAS): No (N/A)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.47 (t, J = 7.4 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.32 (t, J = 7.7 Hz, 1H), 6.97 (d, J = 7.1 Hz, 1H), 6.90 – 6.83 (m, 2H), 4.12 (s, 2H), 1.15 (s, 9H), 0.35 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 155.71, 142.56, 141.01, 129.27, 128.89, 128.39, 126.02, 121.94, 120.79, 117.70, 41.77, 25.70, 18.21, -4.42.

HRMS (ESI) Calculated for C₁₉H₂₆OSi ([M+H]⁺): 299.1826, measured: 299.1823.



(25) 3-Methylthiodiphenylmethane: Prepared from **16a** (0.5 mmol, 125.0 mg) and toluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, normal-phase column EtOAc/pentane 10%→40%.

Yield: 48%, colorless oil. The product was obtained from the column as a mixture with 25% bibenzyl. Note: in order to obtain the spectrum for characterization, two additional reverse-phase column purifications were performed (MeOH/H₂O with 0.1% TFA 89%→100%), which led to considerable mass loss.

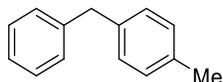
Readily Purchasable (CAS): No (N/A)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.29 (t, J = 7.5 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.12 – 7.08 (m, 2H), 6.96 (d, J = 7.5 Hz, 1H), 3.96 (s, 2H), 2.46 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 141.75, 140.66, 138.45, 128.90, 128.48, 127.11, 126.16, 125.78, 124.20, 41.81, 29.70, 15.78.

HRMS (ESI) Calculated for C₁₄H₁₄S ([M+H]⁺): 215.0889, measured: 215.0888.



(26) 4-Methyldiphenylmethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and *p*-xylene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

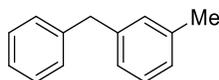
Yield: 82% (61%, 55.5 mg), colorless oil.

Readily Purchasable (CAS): Yes (620-83-7)

Spectra Available in the Literature: Yes⁶

¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 7.13 – 7.07 (m, 4H), 3.96 (s, 2H), 2.33 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 141.40, 138.06, 135.53, 129.13, 128.85, 128.79, 128.41, 125.96, 41.51, 21.00.



(27) 3-Methyldiphenylmethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and *m*-xylene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

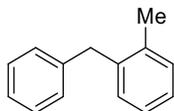
Yield: 85% (59%, 53.7 mg), colorless oil.

Readily Purchasable (CAS): Yes (620-47-3)

Spectra Available in the Literature: Yes⁷

¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.16 (m, 4H), 7.05 – 6.99 (m, 3H), 3.96 (s, 2H), 2.33 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 141.24, 141.01, 138.02, 129.70, 128.91, 128.42, 128.33, 126.81, 125.99, 125.96, 41.89, 21.41.



(28) 2-Methyldiphenylmethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and *o*-xylene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

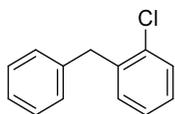
Yield: 84% (60%, 54.6 mg), colorless oil.

Readily Purchasable (CAS): Yes (713-36-0)

Spectra Available in the Literature: Yes⁷

¹H NMR (500 MHz, CDCl₃) δ 7.28 (t, J = 7.6 Hz, 2H), 7.22 – 7.09 (m, 7H), 4.00 (s, 2H), 2.25 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 140.37, 138.90, 136.62, 130.26, 129.92, 128.72, 128.36, 126.43, 125.96, 125.89, 39.43, 19.67.



(29) 2-Chlorodiphenylmethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and 2-chlorotoluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 85%→100%, extraction with 90% pentane/Et₂O.

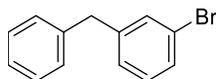
Yield: 63%, slightly yellow oil. The product was obtained from the column as a mixture with <10% bibenzyl.

Readily Purchasable (CAS): Yes (29921-41-3)

Spectra Available in the Literature: Yes¹¹

¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.37 (m, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.25 – 7.13 (m, 6H), 4.12 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 139.49, 138.66, 134.22, 131.00, 129.51, 128.93, 128.45, 127.63, 126.80, 126.22, 39.17.



(30) 3-Bromodiphenylmethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and 3-bromotoluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

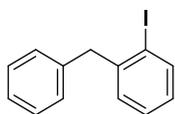
Yield: 65% (58%, 71.6 mg), colorless oil.

Readily Purchasable (CAS): Yes (27798-39-6)

Spectra Available in the Literature: Yes¹²

¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.28 (m, 4H), 7.23 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 7.3 Hz, 2H), 7.17 – 7.10 (m, 2H), 3.95 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 143.43, 140.15, 131.90, 129.99, 129.22, 128.90, 128.60, 127.56, 126.37, 122.54, 41.53.



(31) 2-Iododiphenylmethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and 2-iodotoluene (0.3 M, 1.6 mL) according to Section III.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

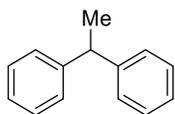
Yield: 57% (50%, 71.6 mg), colorless oil.

Readily Purchasable (CAS): No (35444-93-0)

Spectra Available in the Literature: Yes¹³

¹H NMR (500 MHz, CDCl₃) δ 7.87 (dd, J = 7.9, 1.3 Hz, 1H), 7.34 – 7.17 (m, 6H), 7.12 (dd, J = 7.6, 1.7 Hz, 1H), 6.92 (td, J = 7.6, 1.7 Hz, 1H), 4.12 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 143.61, 139.55, 138.93, 130.35, 129.08, 128.48, 128.33, 128.01, 126.27, 101.30, 46.48.



(32) 1,1-Diphenylethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and ethylbenzene (5.0 mmol, 612 μL) according to Section IV. Uses phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89%→100%, extraction with 90% pentane/Et₂O.

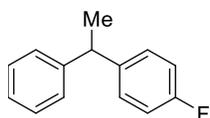
Yield: 69% (60%, 54.6 mg), colorless oil.

Readily Purchasable (CAS): No (612-00-0)

Spectra Available in the Literature: Yes¹³

¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, J = 7.6 Hz, 4H), 7.25 – 7.22 (m, 4H), 7.19 (t, J = 7.2 Hz, 2H), 4.17 (q, J = 7.2 Hz, 1H), 1.66 (d, J = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 146.35, 128.34, 127.61, 126.00, 44.76, 21.85.



(33) 1-(4-Fluorophenyl)-1-phenylethane: Prepared from **1a** (0.5 mmol, 102.1 mg) and 1-ethyl-4-fluorobenzene (5.0 mmol, 625 μ L) according to Section IV. Uses phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89% \rightarrow 100%, extraction with 90% pentane/Et₂O.

Yield: 61%, light yellow oil. The product was obtained from the column as a mixture with 15% biaryl.

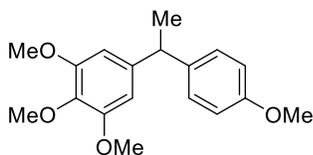
Readily Purchasable (CAS): No (1192278-61-7)

Spectra Available in the Literature: Yes¹⁴

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.26 (m, 2H), 7.22 – 7.15 (m, 5H), 6.97 (t, J = 8.7 Hz, 2H), 4.14 (q, J = 7.2 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 161.26 (d, J = 243.9 Hz), 146.17, 142.04 (d, J = 3.2 Hz), 128.98 (d, J = 7.8 Hz), 128.44, 127.52, 126.15, 115.06 (d, J = 21.1 Hz), 44.04, 22.03.

¹⁹F NMR (377 MHz, CDCl₃) δ -117.54.



(34) 1-(3,4,5-Trimethoxyphenyl)-1-(4-methoxyphenyl)ethane: Prepared from **17a** (0.5 mmol, 147.1 mg) and 4-ethylanisole (5.0 mmol, 731 μ L) according to Section IV. Uses phd as the ligand with 3 mol % Cu.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ dichloromethane, normal-phase column EtOAc/pentane 10% \rightarrow 100%.

Yield: 66%, (61%, 91.4 mg), light orange oil.

OR

Prepared from **17a** (1.7 mmol, 500 mg) and 4-ethylanisole (17 mmol, 2.4 mL) according to Section V. Uses phd as the ligand with 3 mol % Cu.

Reaction duration: 24 h. Purification: Removed solvent, SiO₂ plug w/ dichloromethane, normal-phase column EtOAc/pentane 10% \rightarrow 100%.

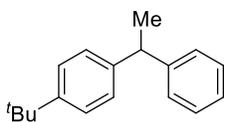
Yield: 70% (64%, 331 mg), light orange oil.

Readily Purchasable (CAS): No (1199256-72-8)

Spectra Available in the Literature: Yes¹⁵

¹H NMR (500 MHz, CDCl₃) δ 7.15 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.42 (s, 2H), 4.04 (q, J = 7.2 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 6H), 3.79 (s, 3H), 1.60 (d, J = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 157.86, 153.02, 142.45, 138.30, 136.15, 128.35, 113.70, 104.57, 60.81, 56.05, 55.22, 44.19, 22.19.



(35) 1-(4-*tert*-Butylphenyl)-1-phenylethane: Prepared from **2a** (0.5 mmol, 130.1 mg) and ethylbenzene (5.0 mmol, 612 μ L) according to Section IV. Uses phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89% \rightarrow 100%, extraction with 90% pentane/Et₂O.

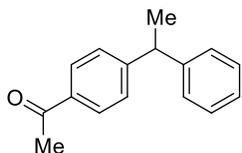
Yield: 70% (62%, 73.8 mg), colorless oil.

Readily Purchasable (CAS): No (94788-62-2)

Spectra Available in the Literature: Yes¹⁶

¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (m, 4H), 7.25 – 7.22 (m, 2H), 7.20 – 7.14 (m, 3H), 4.13 (q, J = 7.2 Hz, 1H), 1.64 (d, J = 7.2 Hz, 3H), 1.30 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 148.67, 146.58, 143.21, 128.30, 127.60, 127.14, 125.92, 125.19, 44.31, 34.32, 31.38, 21.89.



(36) 1-(4-Acetylphenyl)-1-phenylethane: Prepared from **4a** (0.5 mmol, 136.0 mg) and ethylbenzene (5.0 mmol, 612 μ L) according to Section IV. Uses phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/Pentane 10% \rightarrow 90%. The product was obtained with <10% of arylated bibenzyl product (analogous to **E** in Figure S1). Reverse-phase column chromatography (MeOH/H₂O with 0.1% TFA 89% \rightarrow 100%) was used on that sample to get a pure sample for characterization (with higher yield than the previous method).

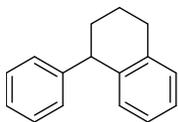
Yield: 56% (50%, 55.9 mg), off-white oil.

Readily Purchasable (CAS): No (94788-60-0)

Spectra Available in the Literature: Yes¹⁷

¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, J = 8.4 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.23 – 7.18 (m, 3H), 4.21 (q, J = 7.2 Hz, 1H), 2.57 (s, 3H), 1.66 (d, J = 7.2 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 197.77, 151.99, 145.30, 135.17, 128.56, 128.51, 127.81, 127.56, 126.35, 44.80, 26.56, 21.53.



(37) 1-Phenyl-1,2,3,4-tetrahydronaphthalene: Prepared from **1a** (0.5 mmol, 102.1 mg) and 1,2,3,4-tetrahydronaphthalene (5.0 mmol, 680 μ L) according to Section IV. Uses phd as the ligand with 3 mol % Cu.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89% \rightarrow 100%, extraction with 90% pentane/Et₂O.

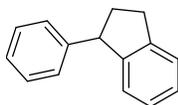
Yield: 50%, colorless oil. The product was obtained from the column as a mixture with <10% of the tetrahydronaphthalene homocoupling product.

Readily Purchasable (CAS): Yes (3018-20-0)

Spectra Available in the Literature: Yes¹⁸

¹H NMR (500 MHz, CDCl₃) δ 7.28 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.17 – 7.09 (m, 4H), 7.07 – 7.00 (m, 1H), 6.84 (d, J = 7.7 Hz, 1H), 4.12 (t, J = 6.8 Hz, 1H), 2.99 – 2.80 (m, 2H), 2.23 – 2.12 (m, 1H), 1.96 – 1.83 (m, 2H), 1.84 – 1.70 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 147.50, 139.36, 137.57, 130.16, 128.93, 128.82, 128.19, 125.91, 125.87, 125.60, 45.61, 33.24, 29.77, 20.95.



(38) 1-Phenylindane: Prepared from **1a** (0.5 mmol, 102.1 mg) and indane (5.0 mmol, 613 μ L) according to Section IV. Uses phd as the ligand with 3 mol % Cu.

Reaction duration: 48 h. Purification: Removed solvent, SiO₂ plug w/ 100:1 pentane/EtOAc, reverse-phase column MeOH/H₂O with 0.1% TFA 89% \rightarrow 100%, extraction with 90% pentane/Et₂O.

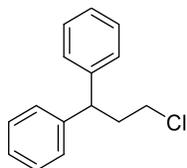
Yield: 65%, colorless oil. The product was obtained from the column as a mixture with 35% of the indane homocoupling product.

Readily Purchasable (CAS): No (26461-03-0)

Spectra Available in the Literature: Yes¹⁹

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.28 (m, 4H), 7.22 – 7.10 (m, 4H), 6.96 (d, J = 7.4 Hz, 1H), 4.34 (t, J = 8.3 Hz, 1H), 3.06 (ddd, J = 15.8, 8.6, 3.7 Hz, 1H), 3.00 – 2.88 (m, 1H), 2.68 – 2.54 (m, 1H), 2.13 – 2.01 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 146.82, 145.39, 144.31, 128.43, 128.09, 126.51, 126.34, 126.32, 124.89, 124.32, 51.63, 36.55, 31.82.



(39) 1-Chloro-3,3-diphenylpropane: Prepared from **1a** (0.5 mmol, 102.1 mg) and 1-chloro-3-phenylpropane (5.0 mmol, 716 μ L) according to Section IV. Uses less chlorobenzene (100 μ l, 5.0M) and more di-*tert*-butyl peroxide (3.0 mmol, 549 μ L, 6.0 equiv.), using phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 100:1 pentane/EtOAc, passed over an SiO₂ plug, ran a reverse-phase column with MeOH/H₂O with 0.1% TFA 70% \rightarrow 100%, extraction with 90% pentane/Et₂O.

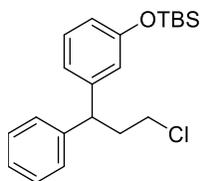
Yield: 61% (42%, 47.9 mg), colorless oil.

Readily Purchasable (CAS): No (29648-95-1)

Spectra Available in the Literature: Yes²⁰

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.27 (m, 4H), 7.28 – 7.24 (m, 4H), 7.21 (t, J = 7.2 Hz, 2H), 4.23 (t, J = 7.8 Hz, 1H), 3.47 (t, J = 6.6 Hz, 2H), 2.51 (dt, J = 7.9, 6.6 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 143.52, 128.62, 127.86, 126.51, 47.87, 43.21, 38.14.



(40) 1-Chloro-3-(3-*tert*-butyldimethylsilyloxyphenyl)-3-phenylpropane: Prepared from **15a** (0.5 mmol, 167.1 mg) and 1-chloro-3-phenylpropane (5.0 mmol, 716 μ L) according to Section IV. Uses less chlorobenzene (100 μ l, 5.0M) and more di-*tert*-butyl peroxide (3.0 mmol, 549 μ L, 6.0 equiv.), using phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 100:1 pentane/EtOAc, passed over an SiO₂ plug, ran a reverse-phase column with MeOH/H₂O with 0.1% TFA 70% \rightarrow 100%, extraction with 90% pentane/Et₂O.

Yield: 52% (41%, 73.5 mg), colorless oil.

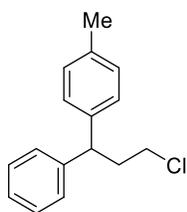
Readily Purchasable (CAS): No (N/A)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.29 (t, J = 6.5 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.14 (t, J = 7.9 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 6.72 (t, J = 2.1 Hz, 1H), 6.68 (ddd, J = 8.0, 2.5, 1.0 Hz, 1H), 4.15 (t, J = 7.8 Hz, 1H), 3.45 (t, J = 6.6 Hz, 2H), 2.47 (dt, J = 7.8, 6.6 Hz, 2H), 0.96 (s, 9H), 0.15 (d, J = 1.5 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 155.78, 145.03, 143.45, 129.45, 128.55, 127.79, 126.47, 120.88, 119.73, 118.14, 47.65, 43.19, 38.04, 25.69, 18.22, -4.41, -4.43.

HRMS (ESI) Calculated for C₂₁H₂₉OCISi ([M+H]⁺): 361.1749, measured: 361.1749



(41) 1-Chloro-3-(*p*-tolyl)-3-phenylpropane: Prepared from **21a** (0.5 mmol, 109.1 mg) and 1-chloro-3-phenylpropane (5.0 mmol, 716 μ L) according to Section IV. Uses less chlorobenzene (100 μ l, 5.0M) and more di-*tert*-butyl peroxide (3.0 mmol, 549 μ L, 6.0 equiv.), using phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 100:1 pentane/EtOAc, passed over an SiO₂ plug, ran a reverse-phase column with MeOH/H₂O with 0.1% TFA 70% \rightarrow 100%, extraction with 90% pentane/Et₂O.

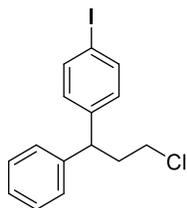
Yield: 45%, white solid. The product was obtained from the column as a mixture with <10% of the 1-chloro-3-phenylpropane homocoupling product.

Readily Purchasable (CAS): No (55707-02-3)

Spectra Available in the Literature: Yes²⁰

¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.08 (m, 9H), 4.17 (t, J = 7.8 Hz, 1H), 3.45 (t, J = 6.6 Hz, 2H), 2.48 (dt, J = 7.9, 6.6 Hz, 2H), 2.30 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 143.79, 140.49, 136.03, 129.29, 128.58, 127.77, 127.70, 126.51, 47.48, 43.22, 38.18, 20.96.



(42) 1-Chloro-3-(4-iodophenyl)-3-phenylpropane: Prepared from **8a** (0.5 mmol, 165 mg) and 1-chloro-3-phenylpropane (5.0 mmol, 716 μ L) according to Section IV. Uses less chlorobenzene (100 μ l, 5.0M) and more di-*tert*-butyl peroxide (3.0 mmol, 549 μ L, 6.0 equiv.), using phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 100:1 pentane/EtOAc, passed over an SiO₂ plug, ran a reverse-phase column with MeOH/H₂O with 0.1% TFA 70% \rightarrow 100%, extraction with 90% pentane/Et₂O.

Yield: 48% (37%, 65.8 mg), off-white oil.

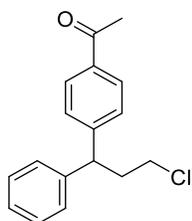
Readily Purchasable (CAS): No (N/A)

Spectra Available in the Literature: No

¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, J = 8.4 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 7.00 (d, J = 8.3 Hz, 2H), 4.18 (t, J = 7.8 Hz, 1H), 3.44 (t, J = 6.5 Hz, 2H), 2.46 (dq, J = 7.8, 6.4 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 143.28, 142.79, 137.66, 129.91, 128.74, 127.76, 126.75, 91.80, 47.30, 42.93, 37.80.

HRMS (ESI) Calculated for C₁₅H₁₄ICl ([M+H]⁺): 355.9823, measured: 355.9820



(43) 1-Chloro-3-(4-acetylphenyl)-3-phenylpropane: Prepared from **4a** (0.5 mmol, 123.1 mg) and 1-chloro-3-phenylpropane (5.0 mmol, 716 μ L) according to Section IV. Uses less chlorobenzene (100 μ l, 5.0M) and more di-*tert*-butyl peroxide (3.0 mmol, 549 μ L, 6.0 equiv.), using phen as the ligand with 5 mol% Cu.

Reaction duration: 48 h. Purification: Removed solvent, syringe filtered w/ 100:1 pentane/EtOAc, passed over an SiO₂ plug w/ 9:1 pentane/EtOAc, normal-phase column EtOAc/pentane 10% \rightarrow 100%.

Yield: 43% (33%, 45 mg), slightly orange solid.

Readily Purchasable (CAS): No (N/A)

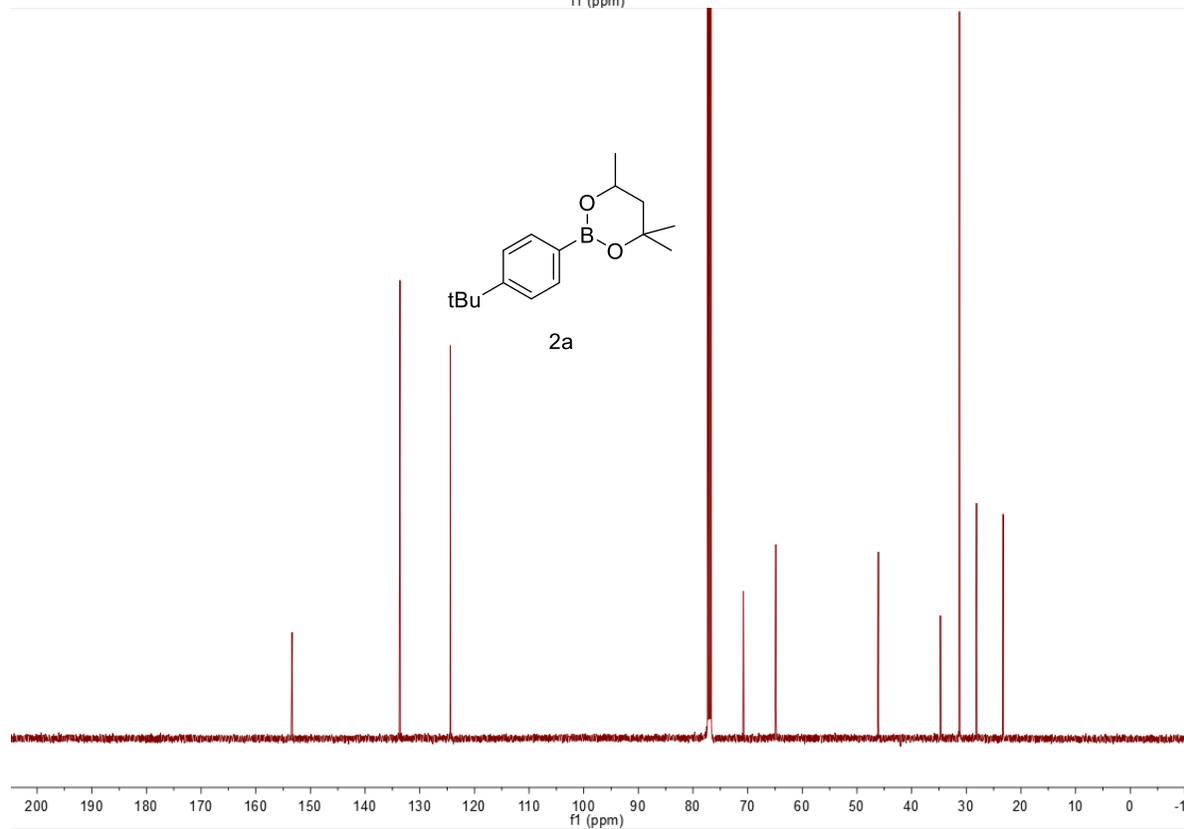
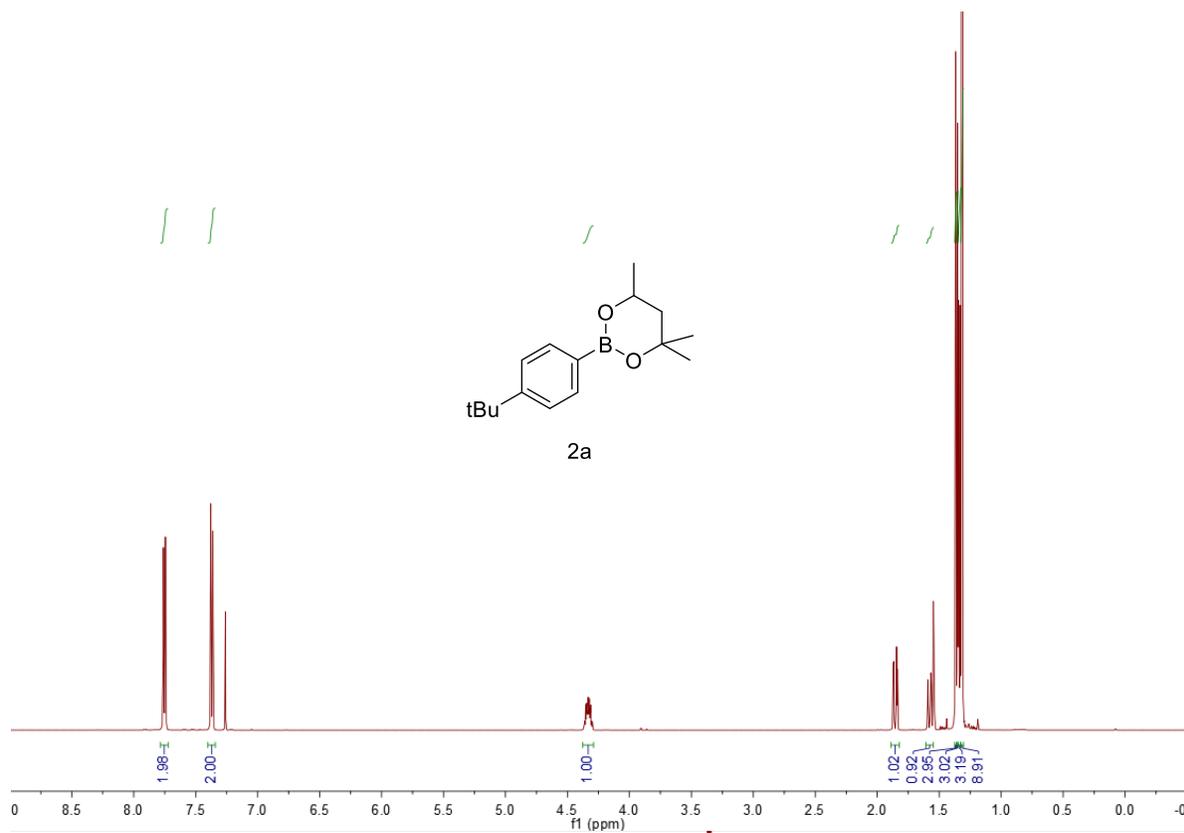
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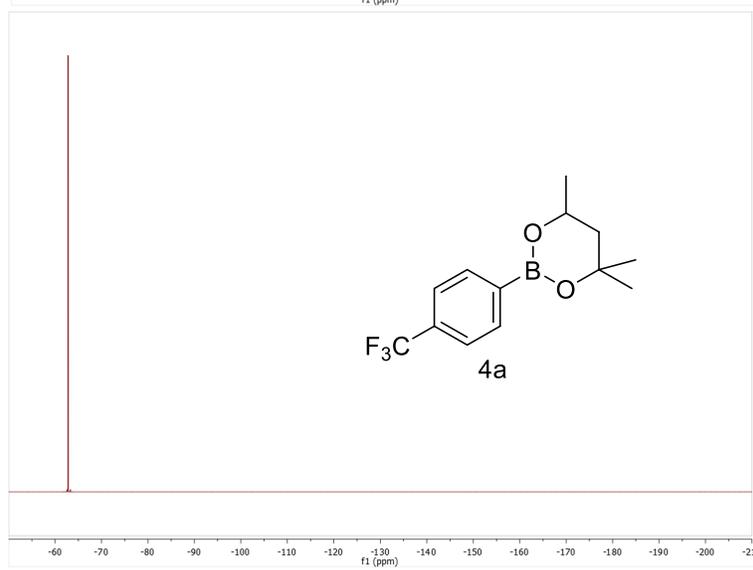
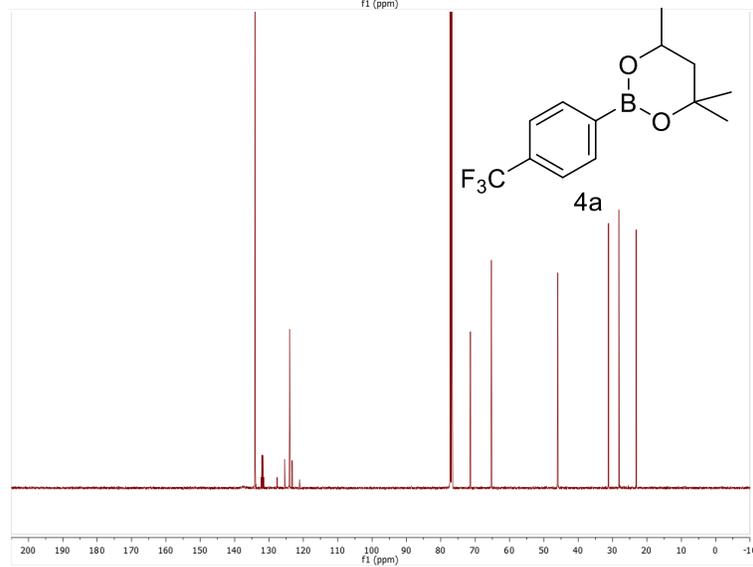
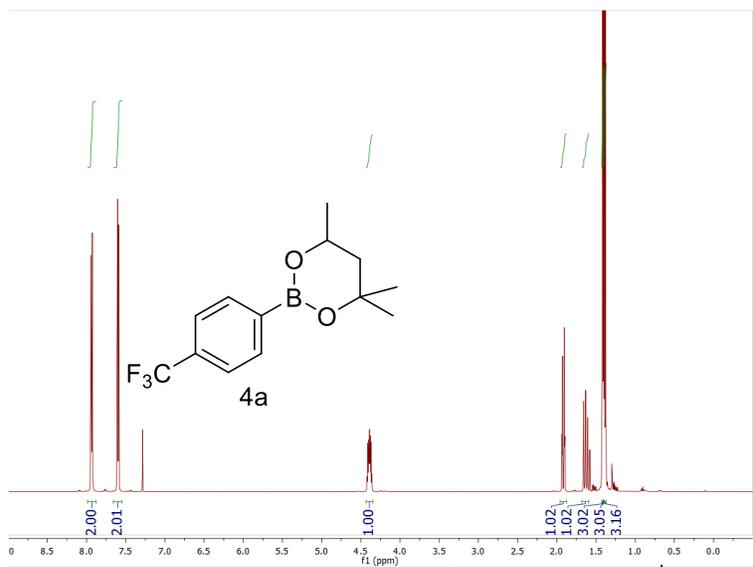
¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 4.30 (t, J = 7.8 Hz, 1H), 3.45 (t, J = 6.5 Hz, 2H), 2.57 (s, 3H), 2.52 (dtd, J = 7.7, 6.5, 3.3 Hz, 2H).

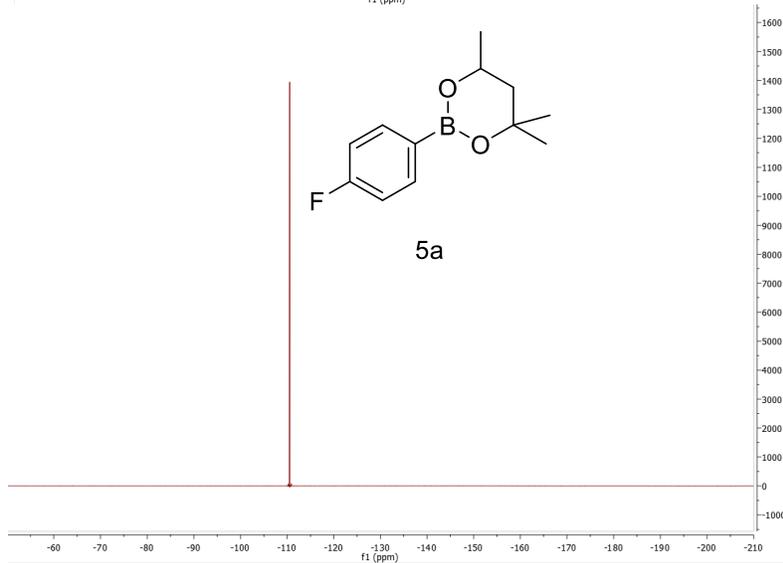
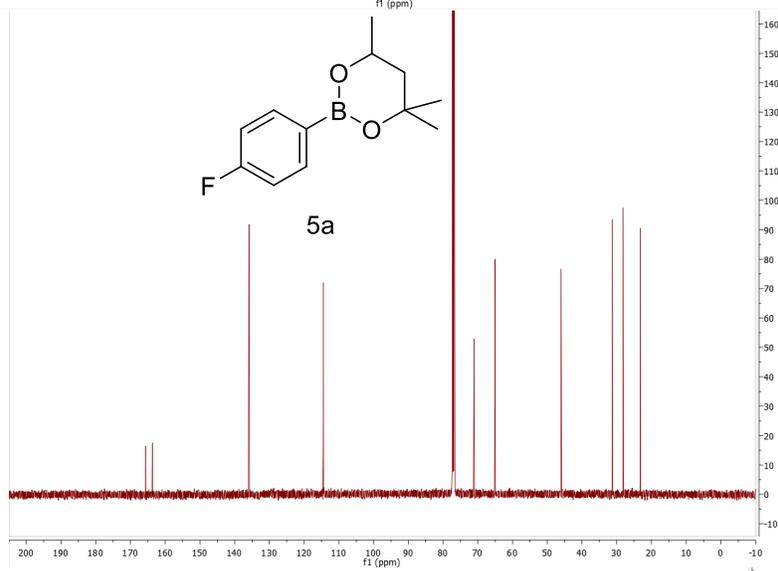
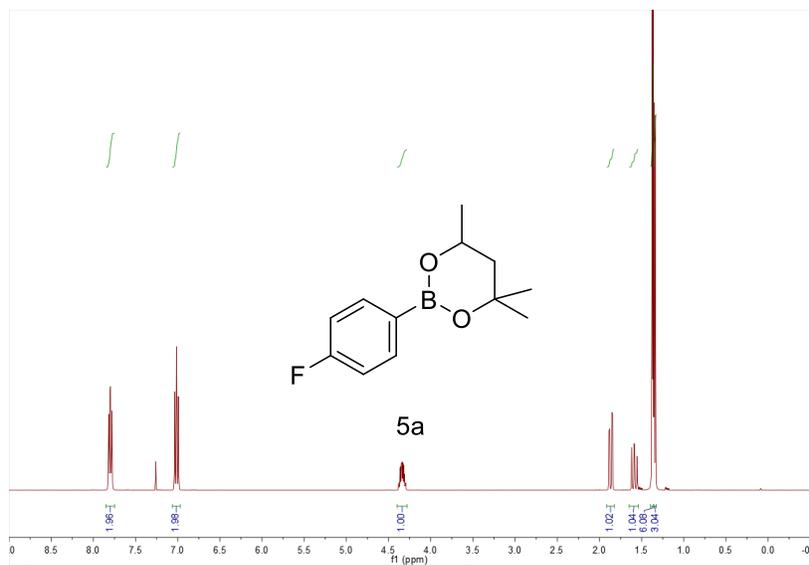
¹³C NMR (126 MHz, CDCl₃) δ 197.62, 149.11, 142.47, 135.57, 128.80, 128.76, 128.07, 127.84, 126.87, 47.76, 42.86, 37.73, 26.57.

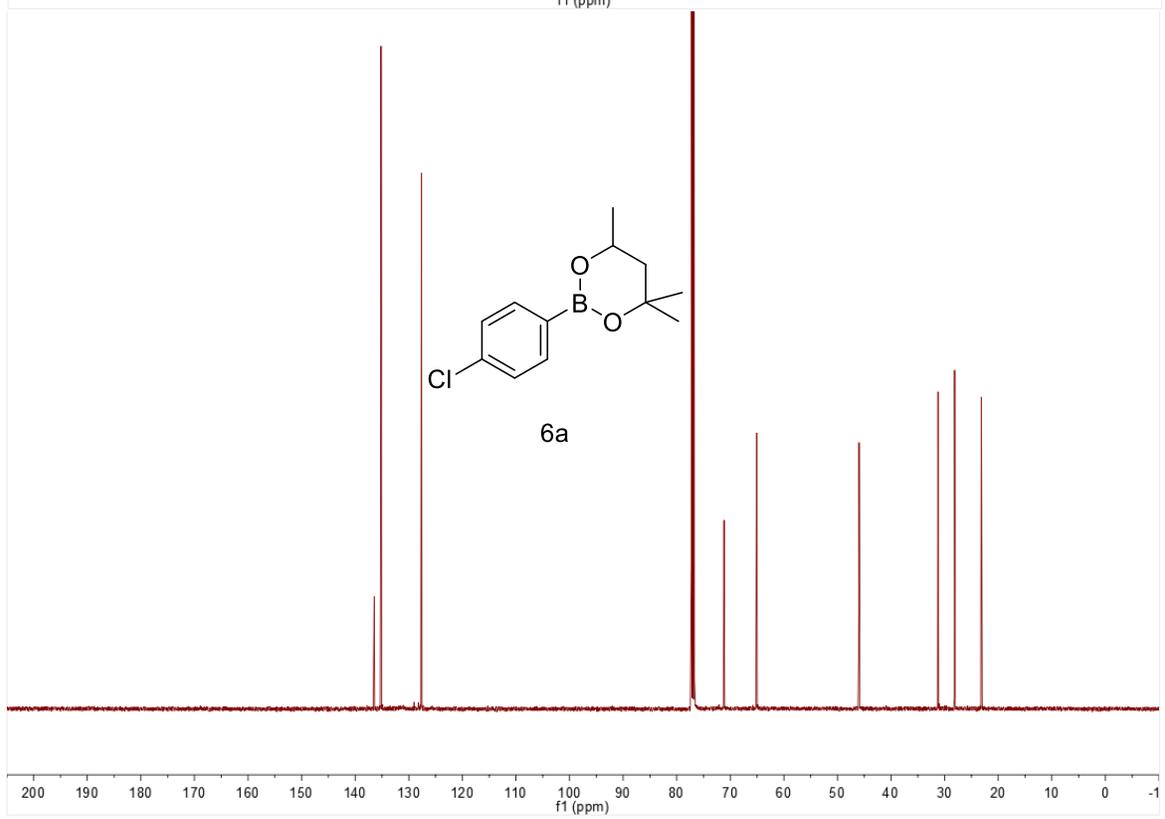
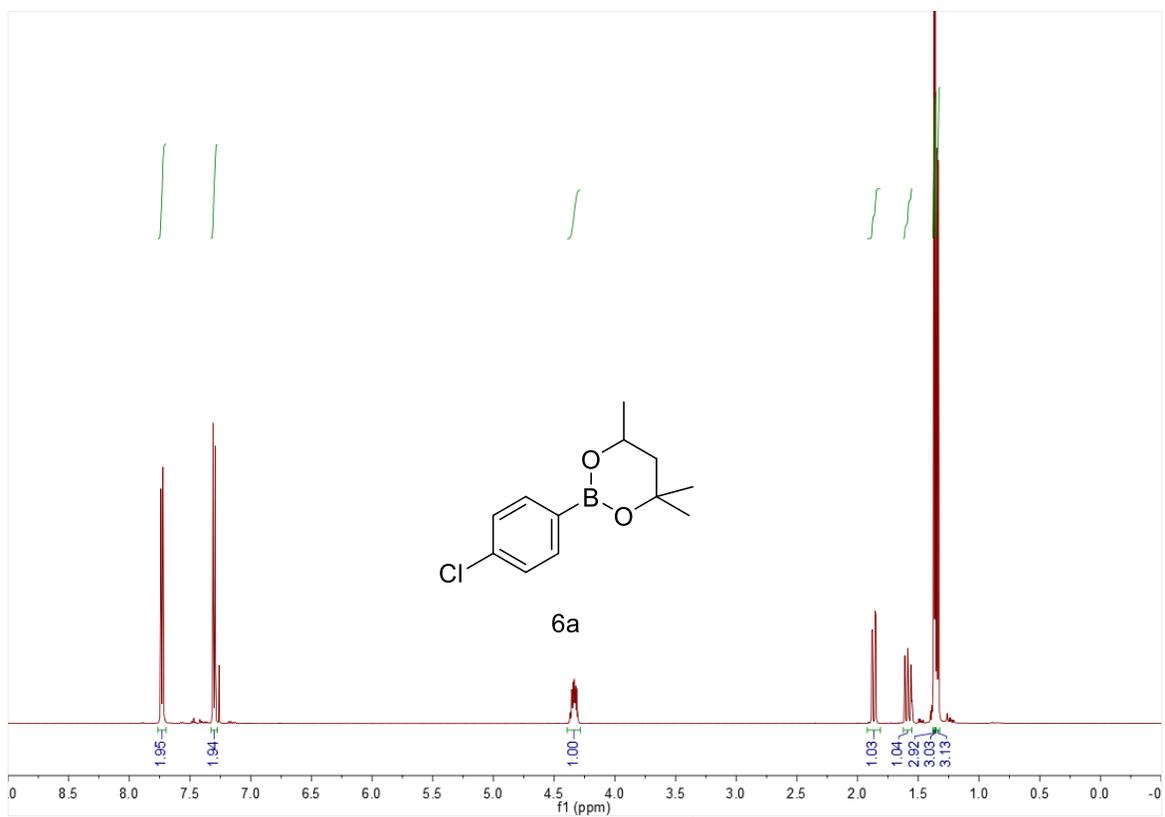
HRMS (ESI) Calculated for C₁₇H₁₇OCl ([M+H]⁺): 273.1041, measured: 273.1041

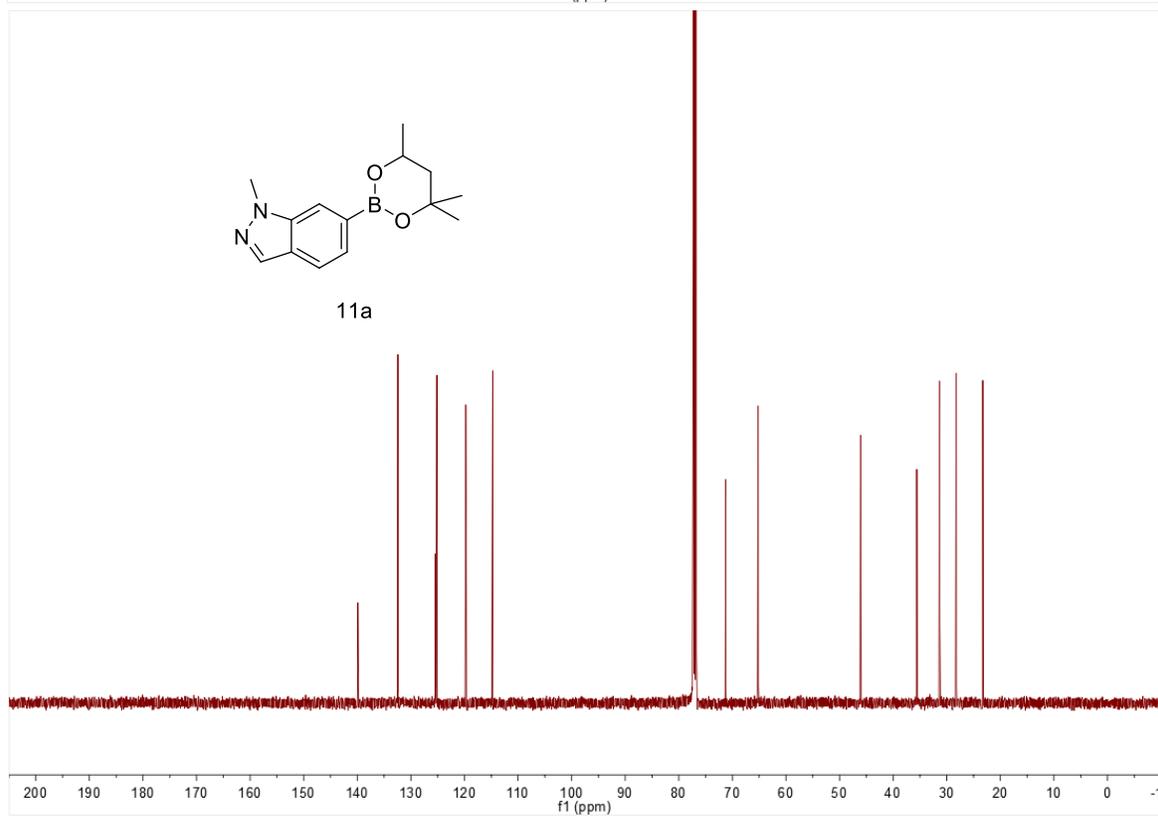
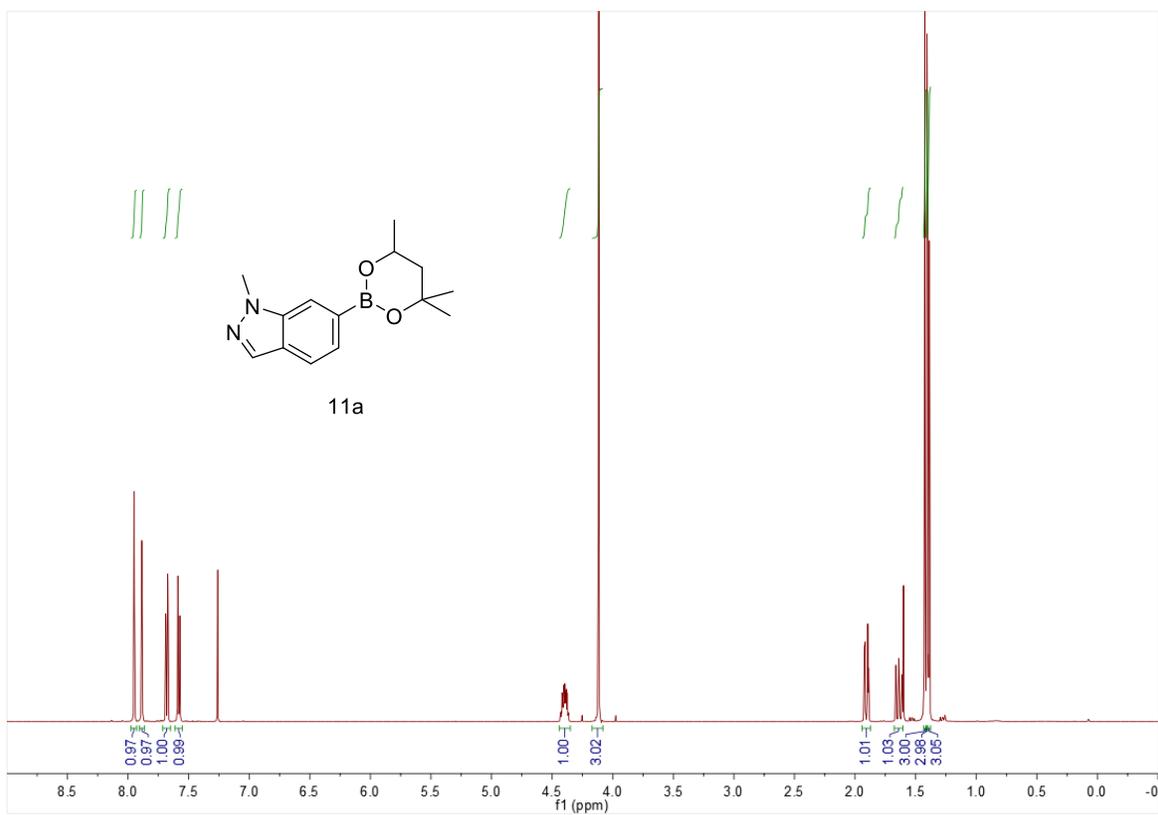
X. ^1H and ^{13}C NMR Spectra

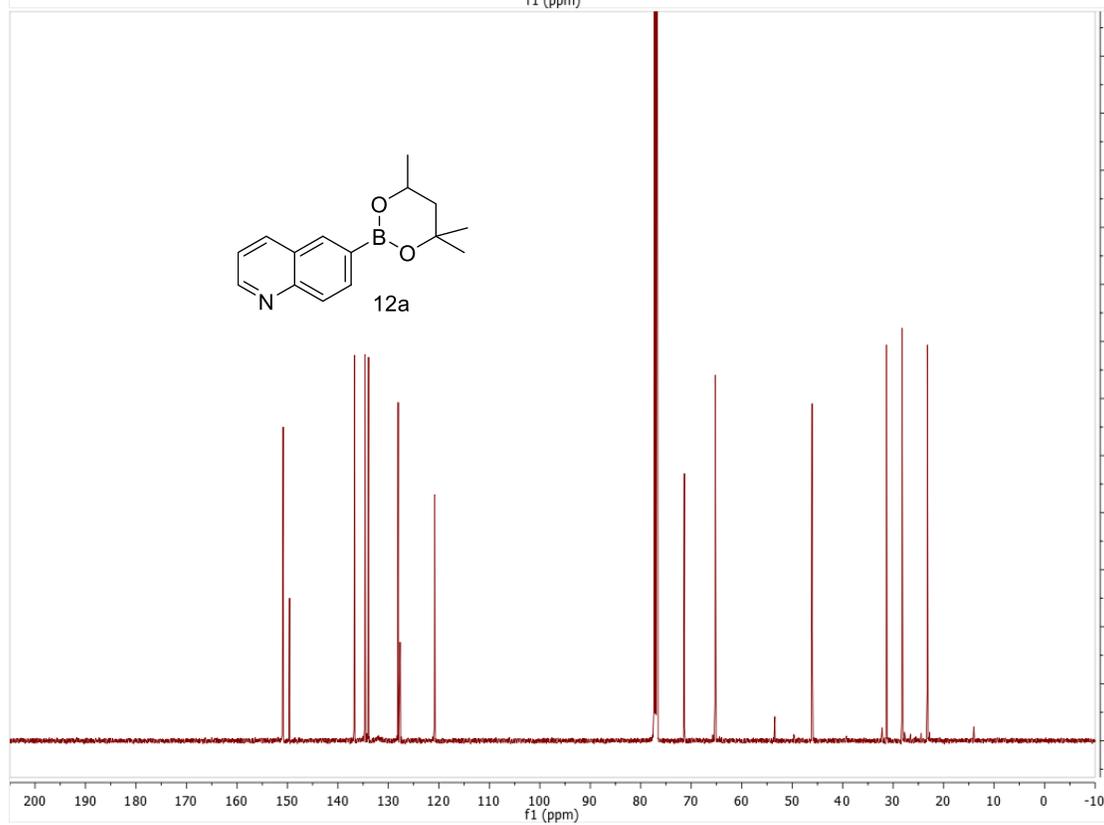
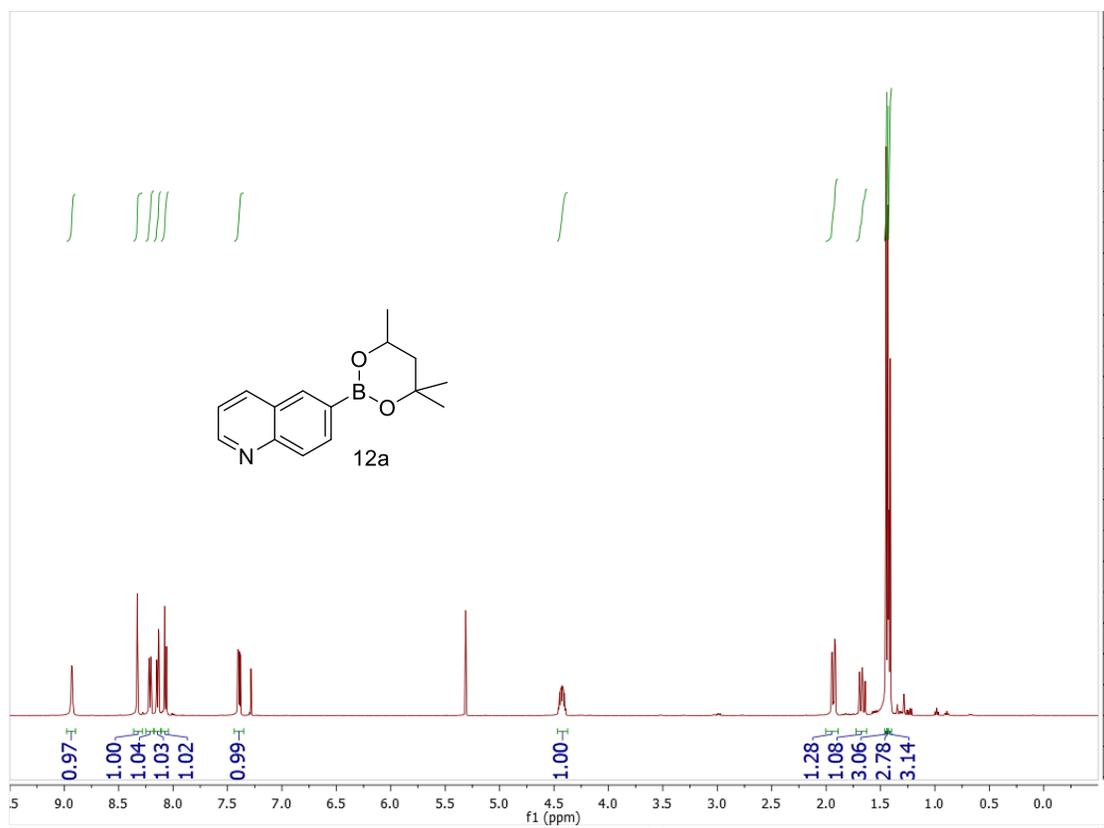


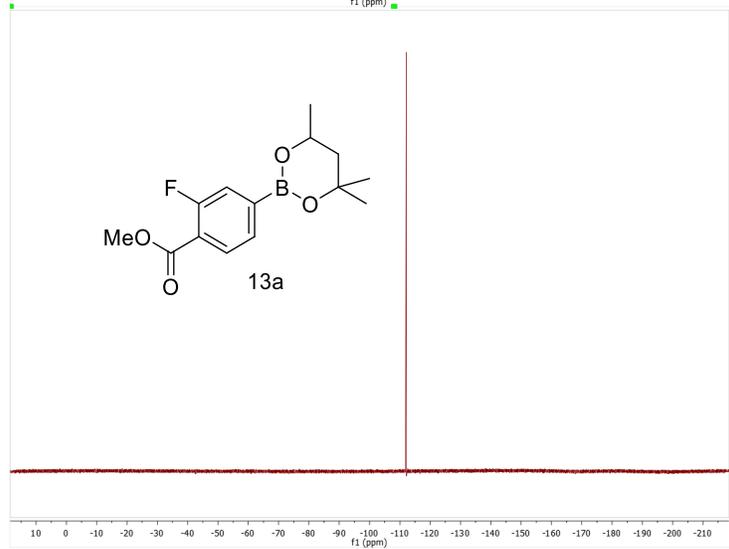
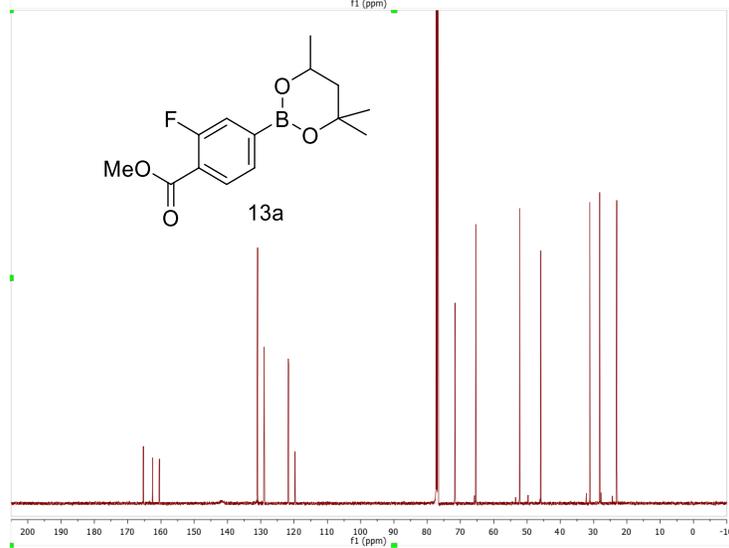
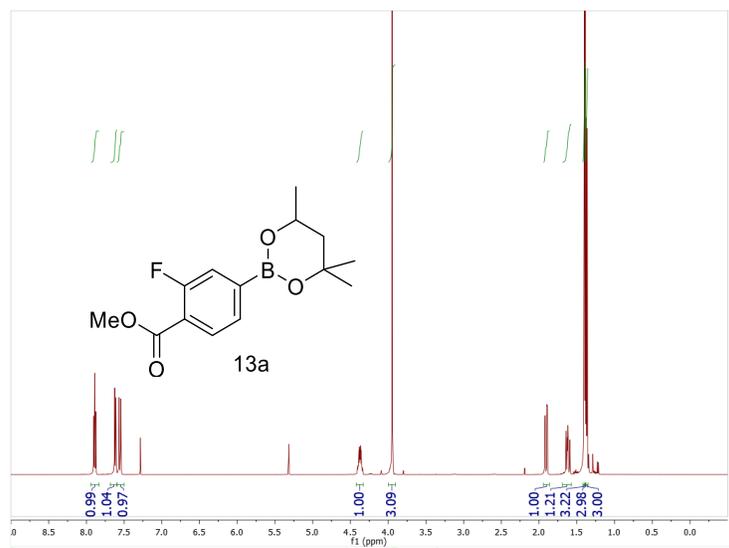


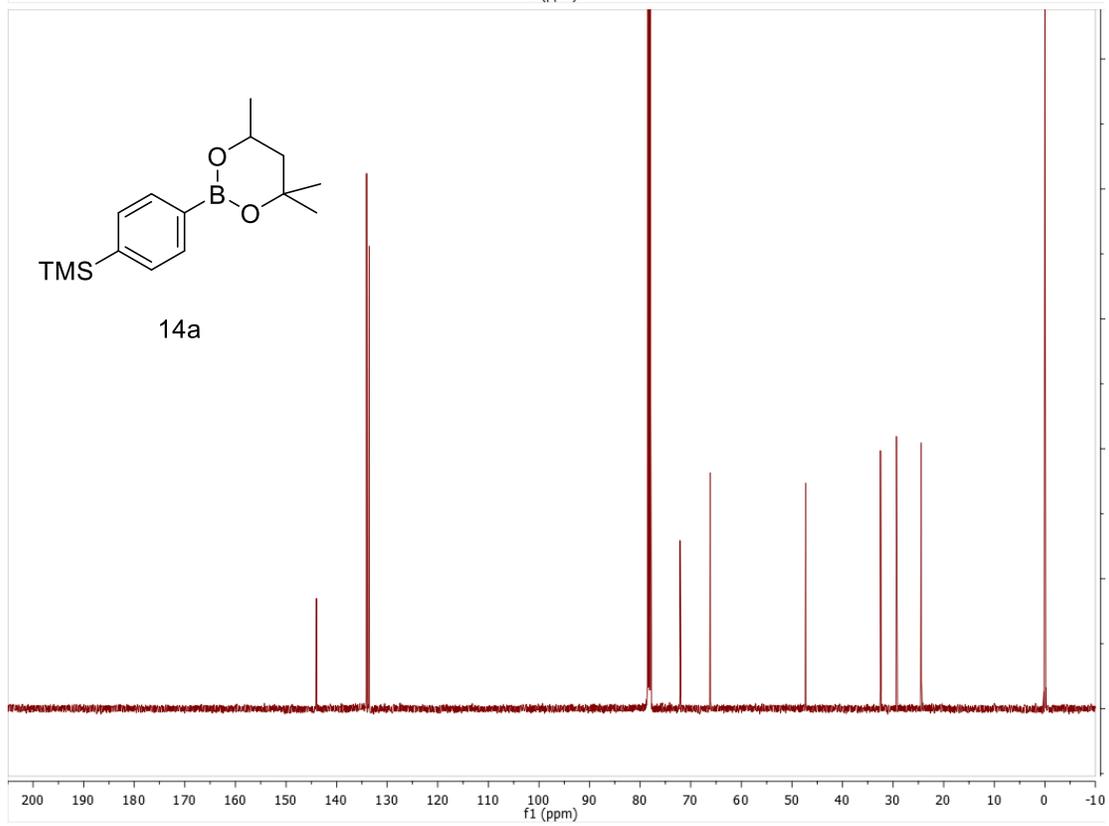
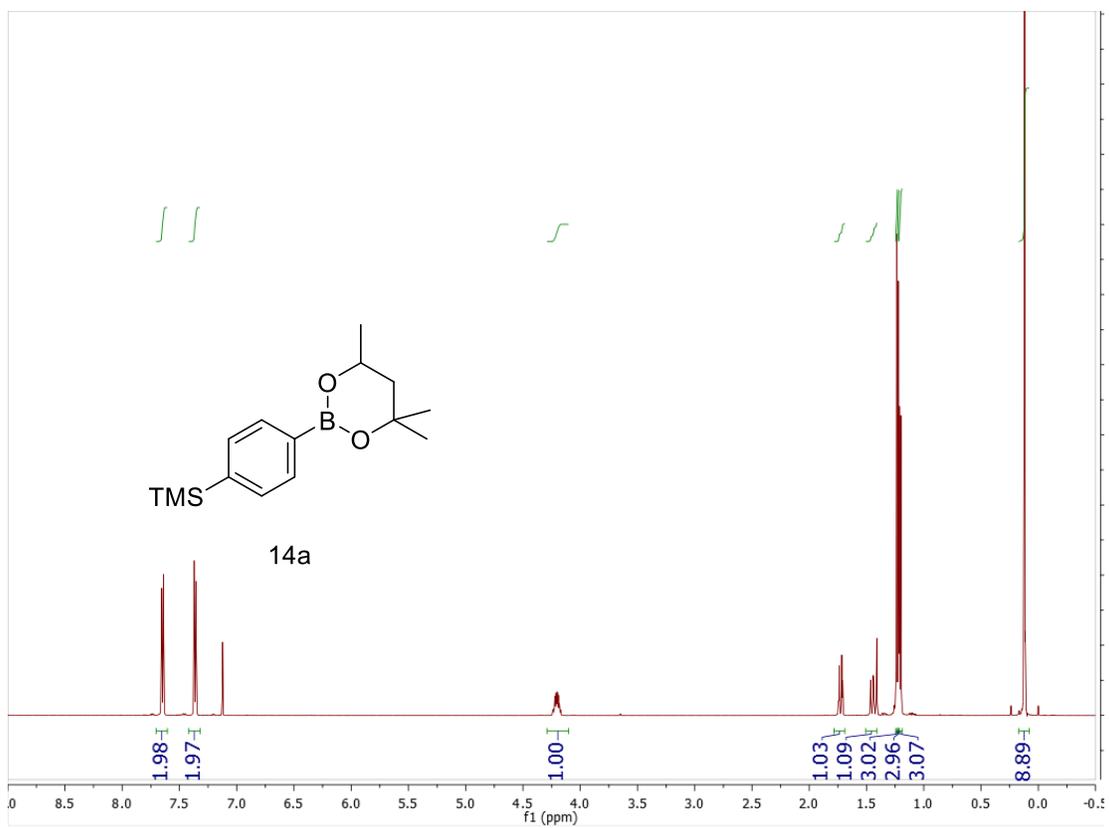


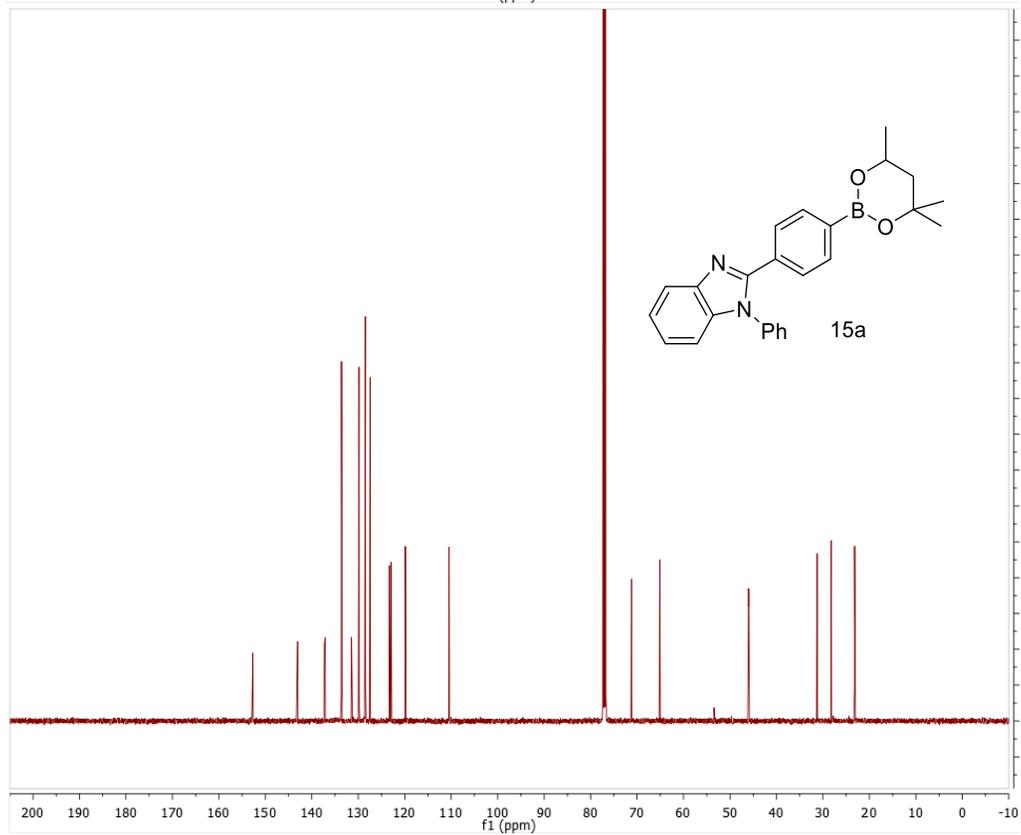
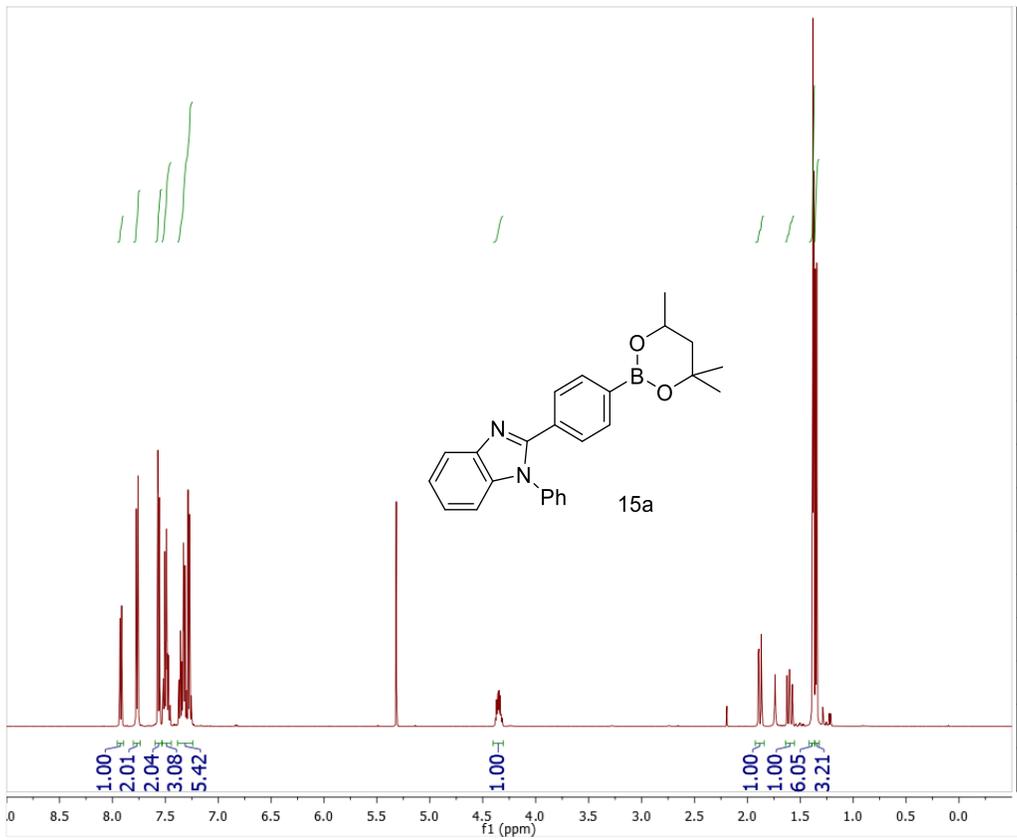


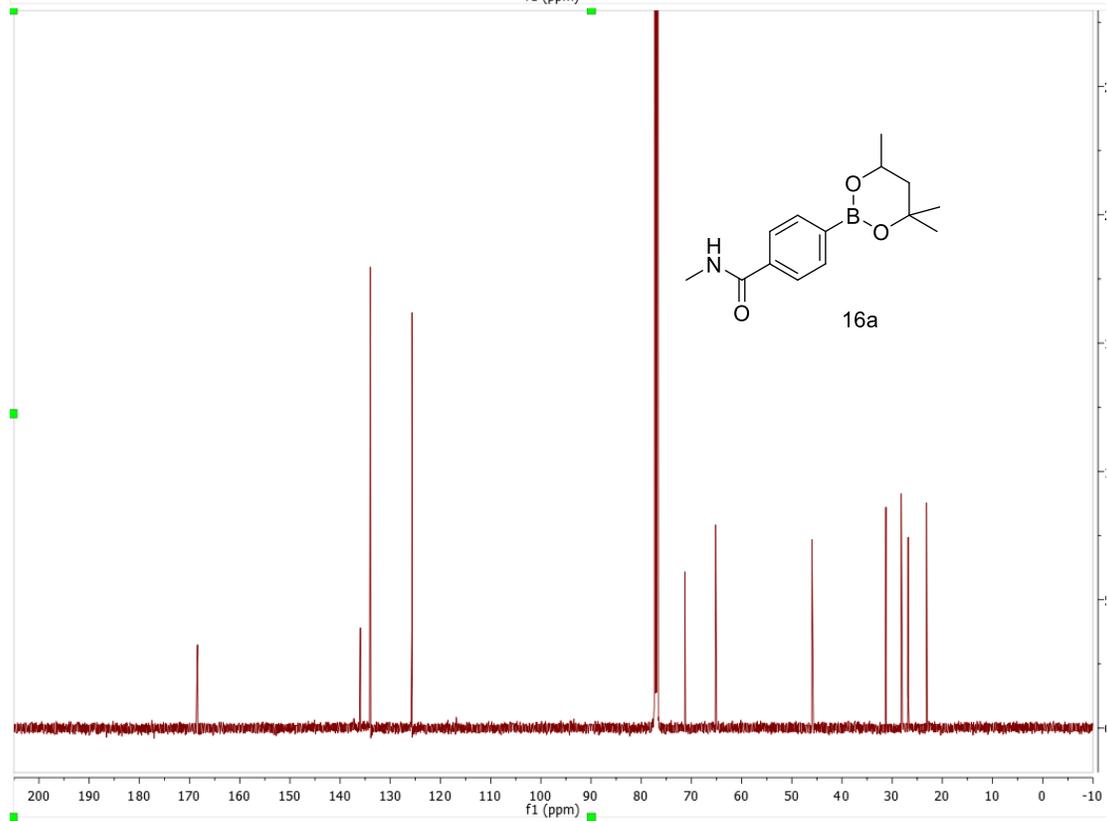
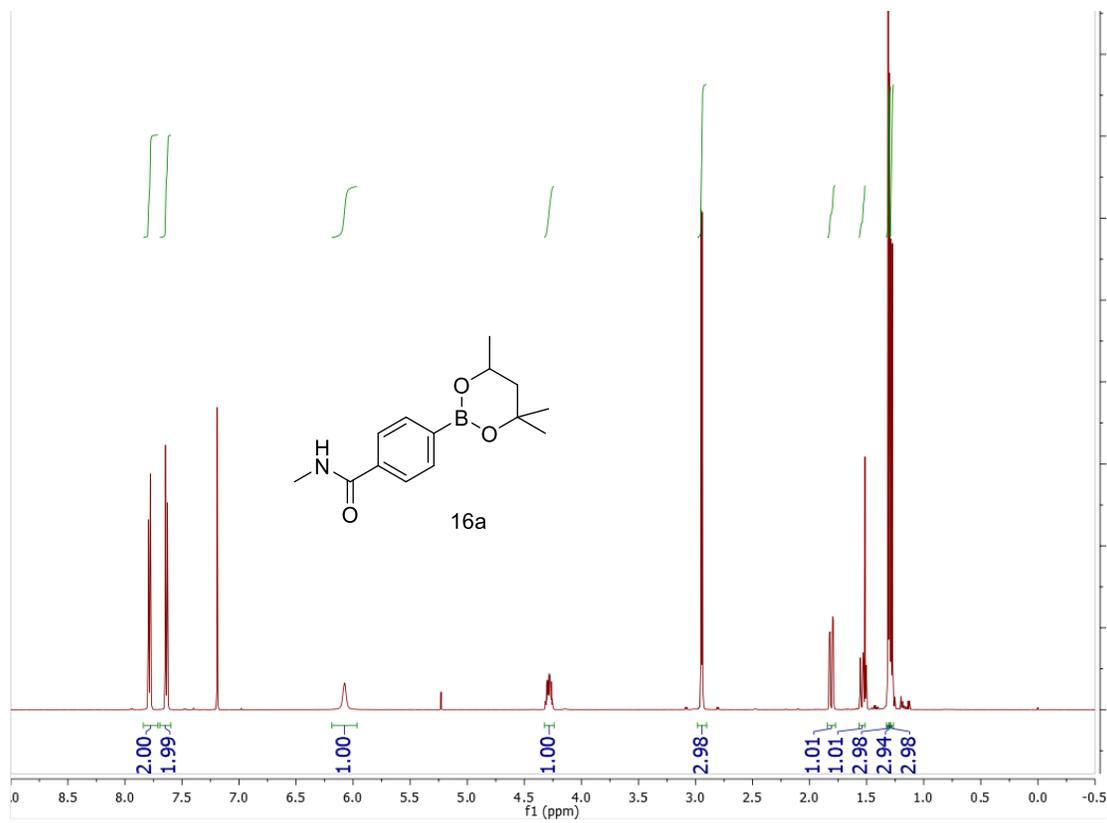


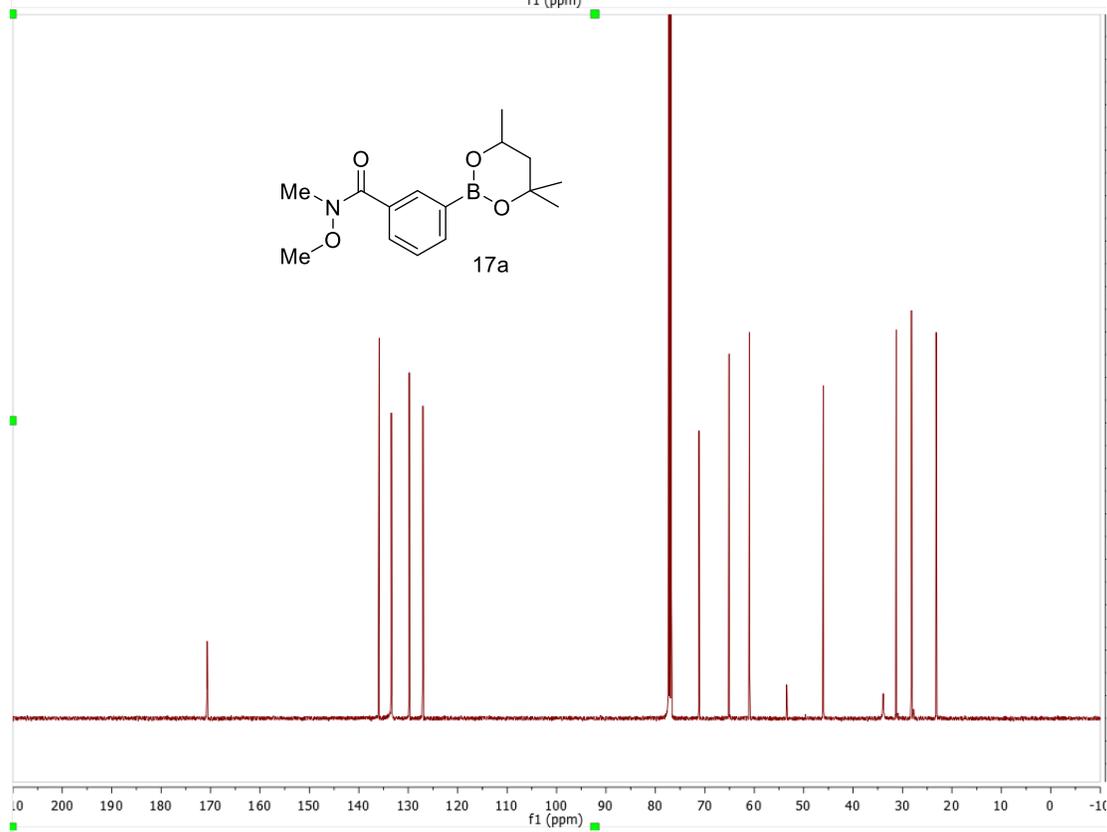
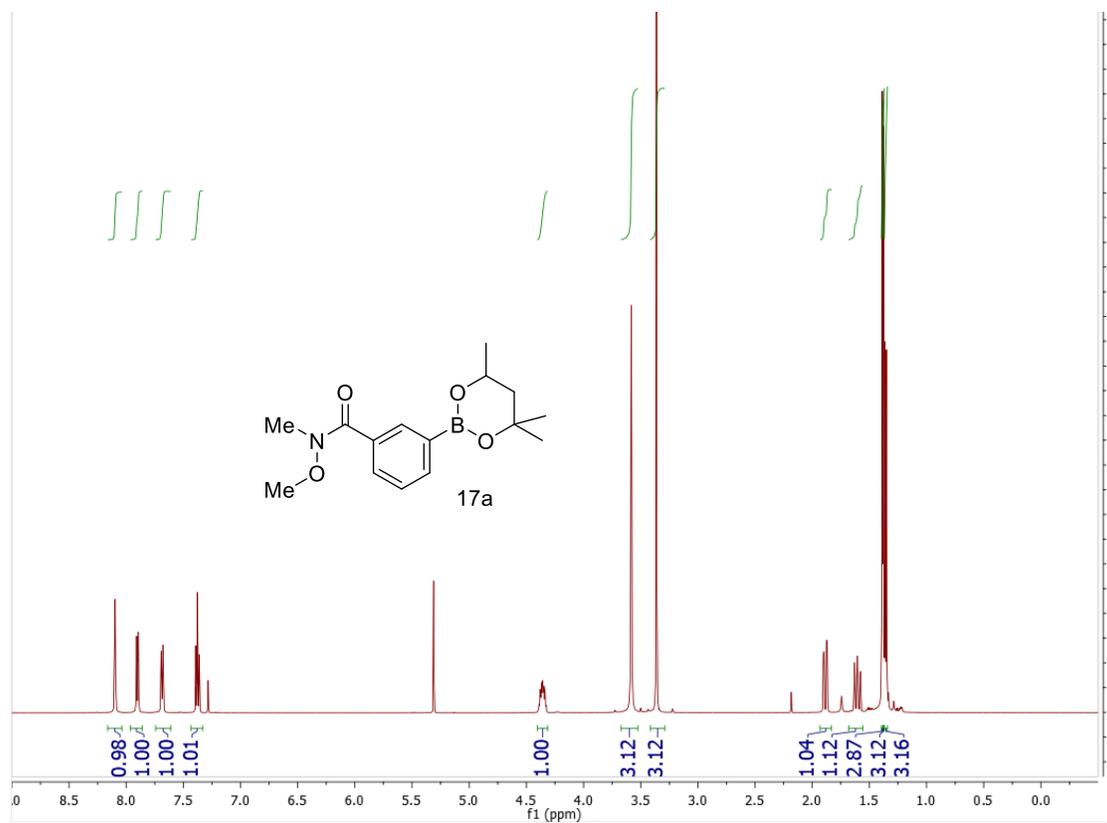


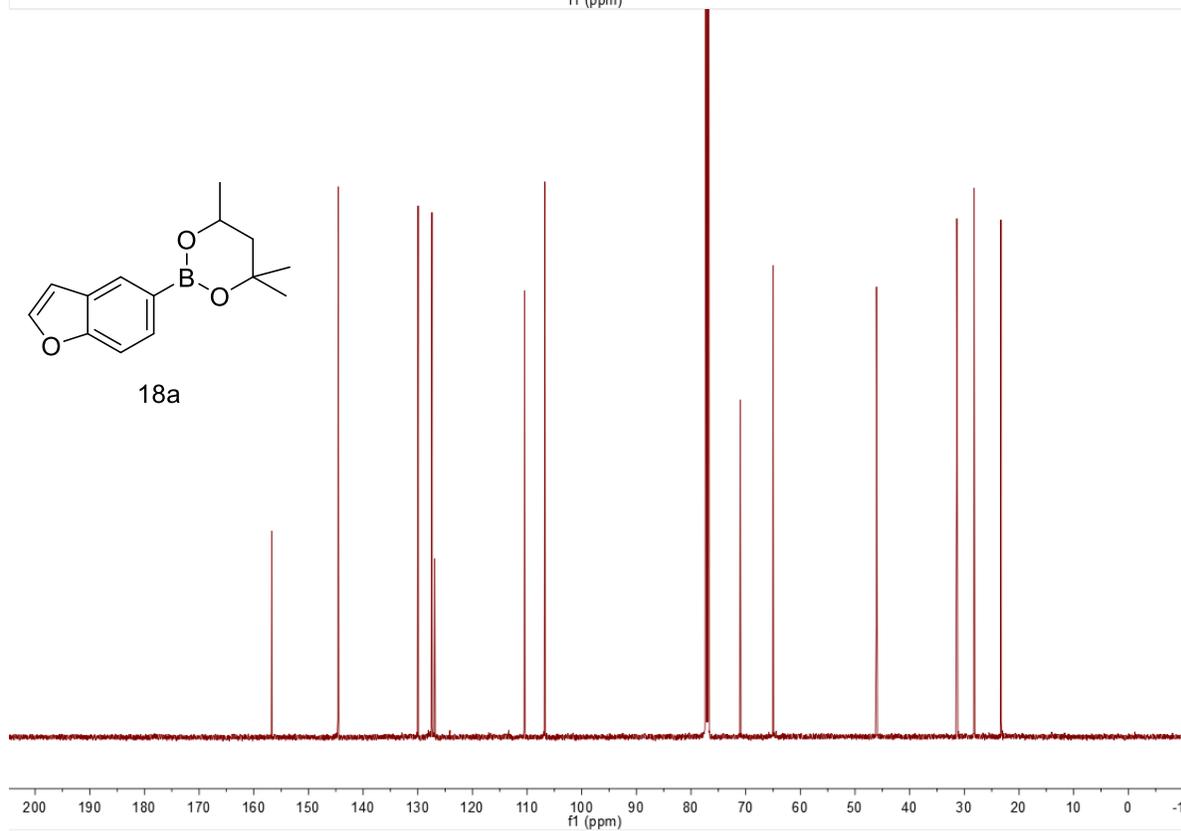
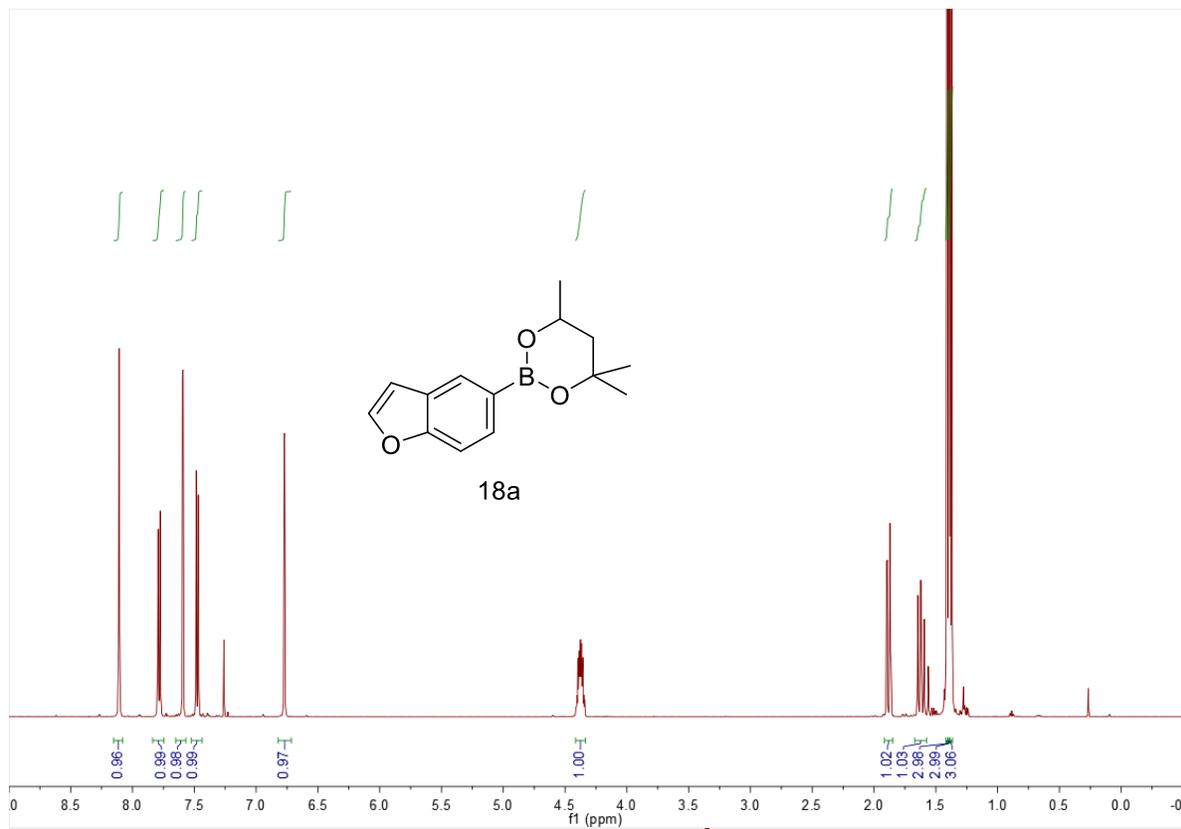


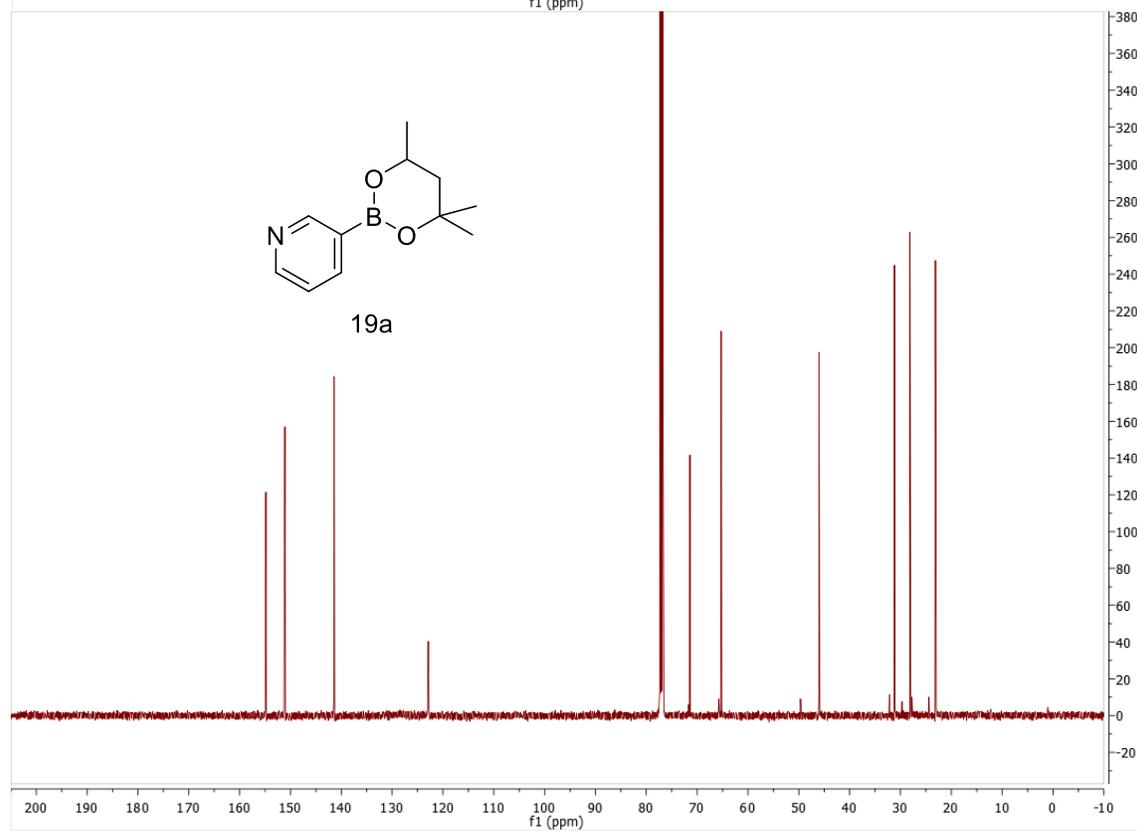
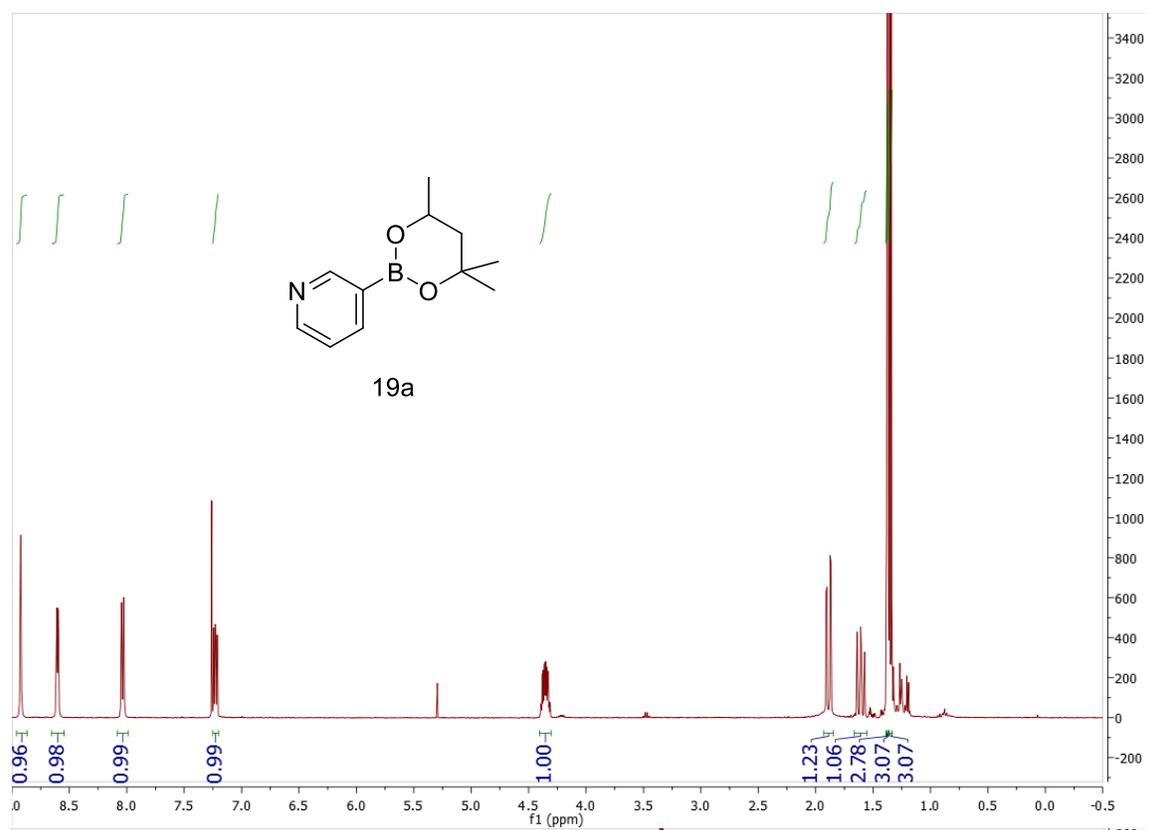


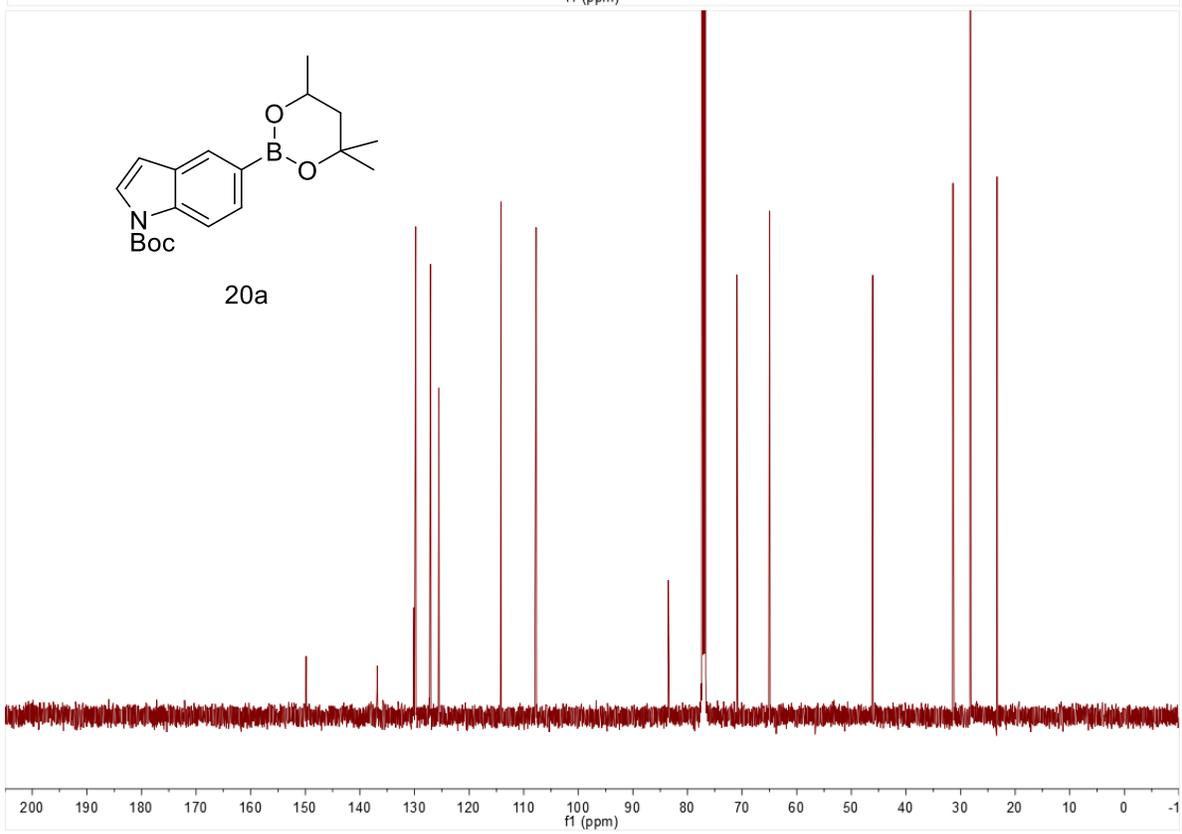
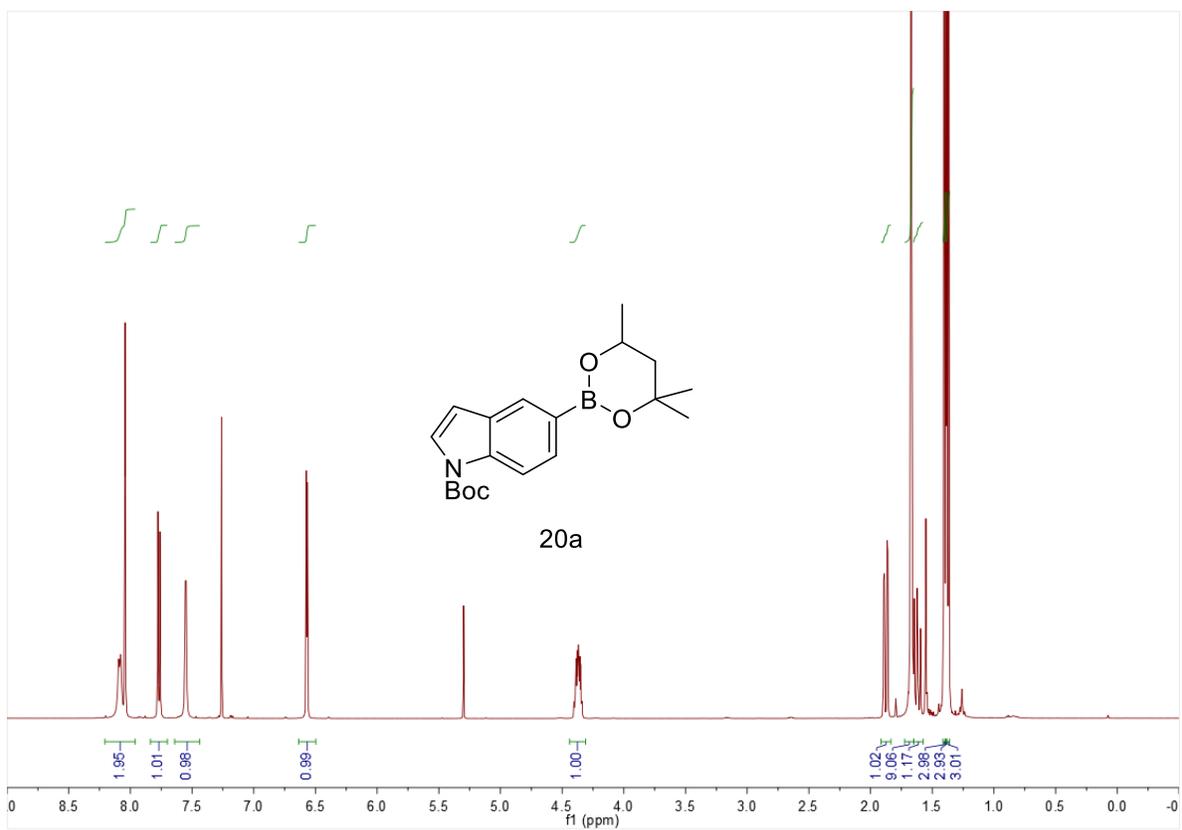


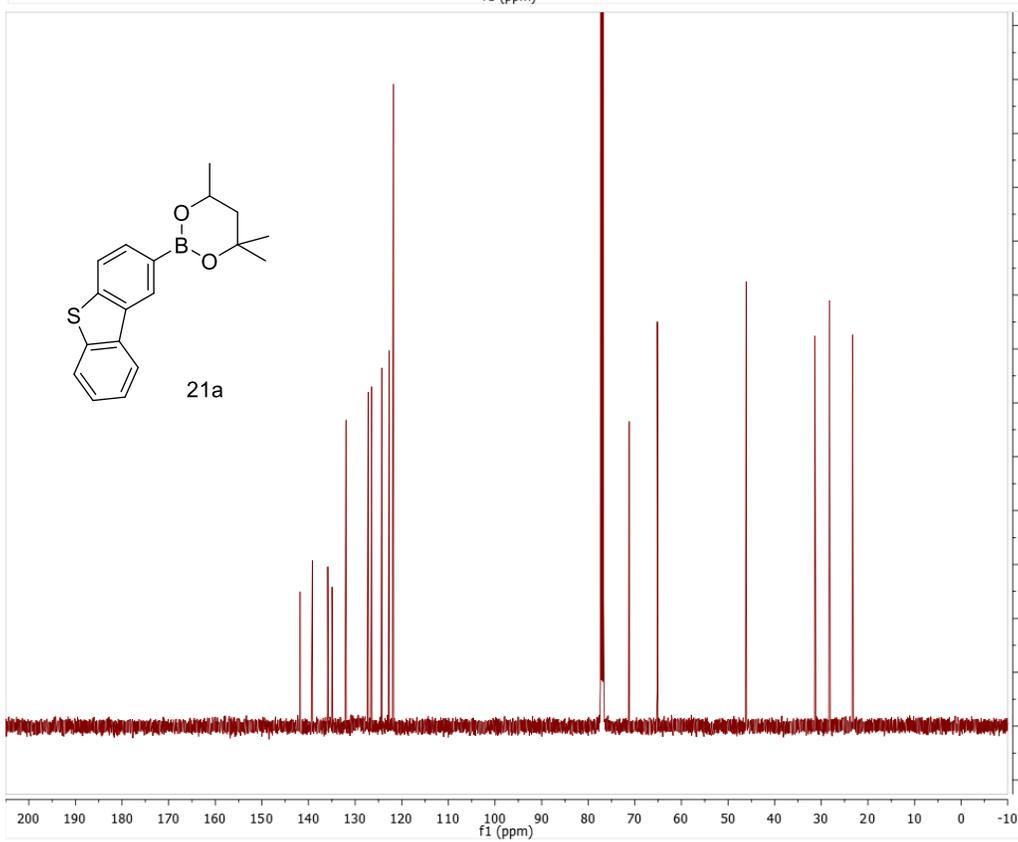
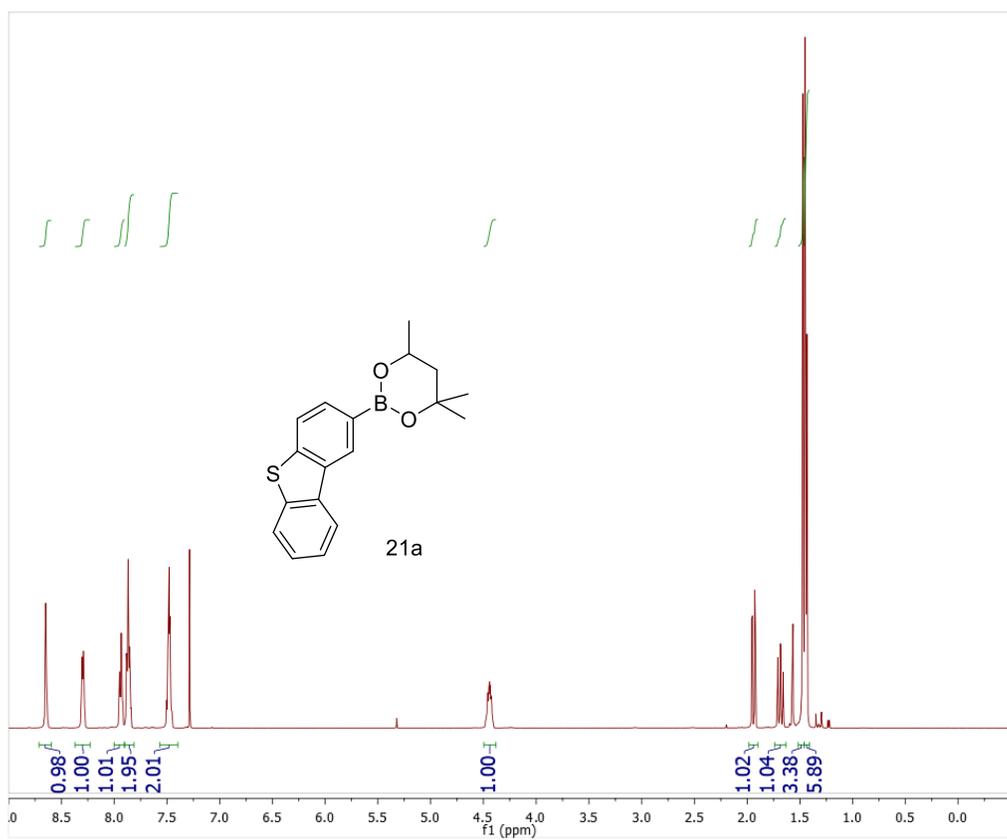


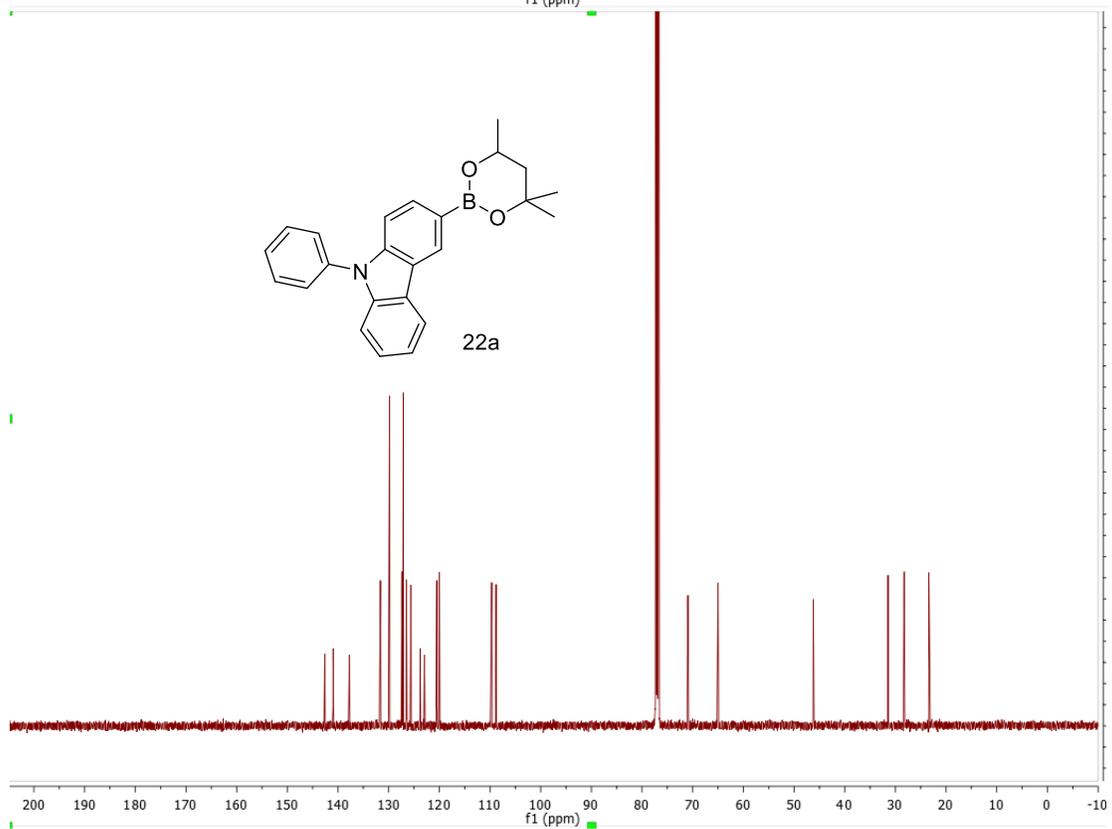
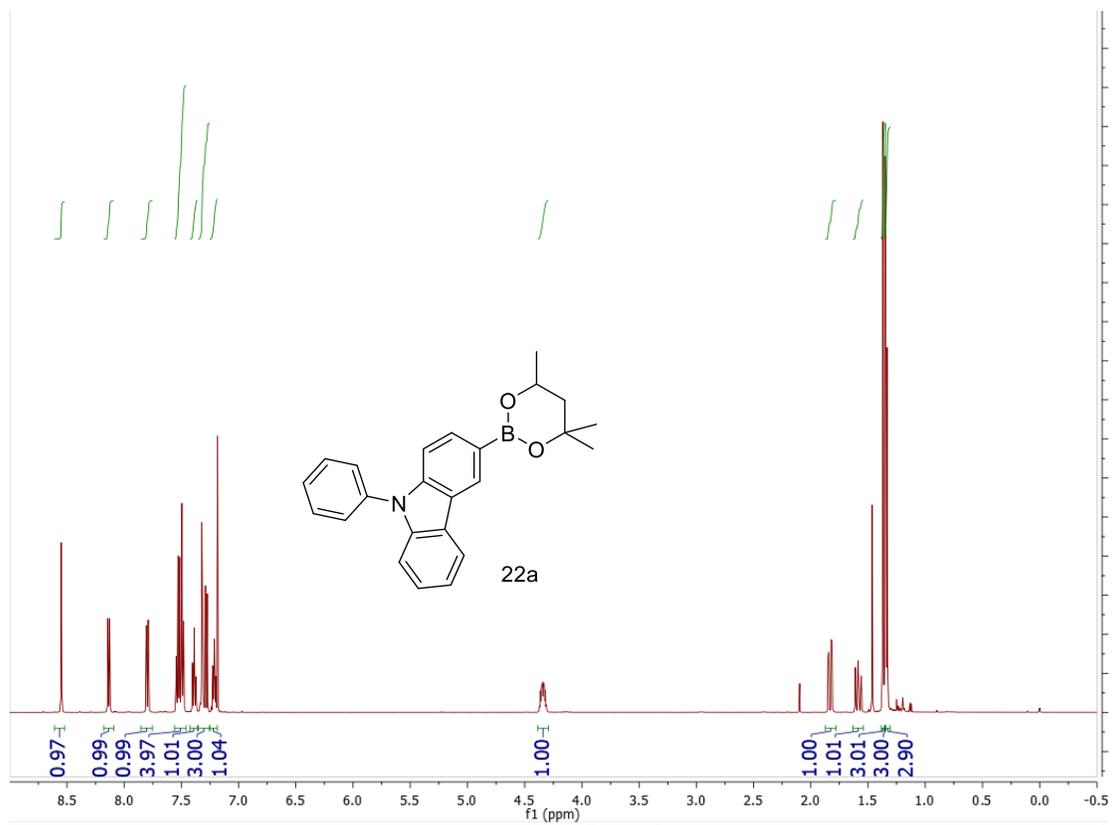


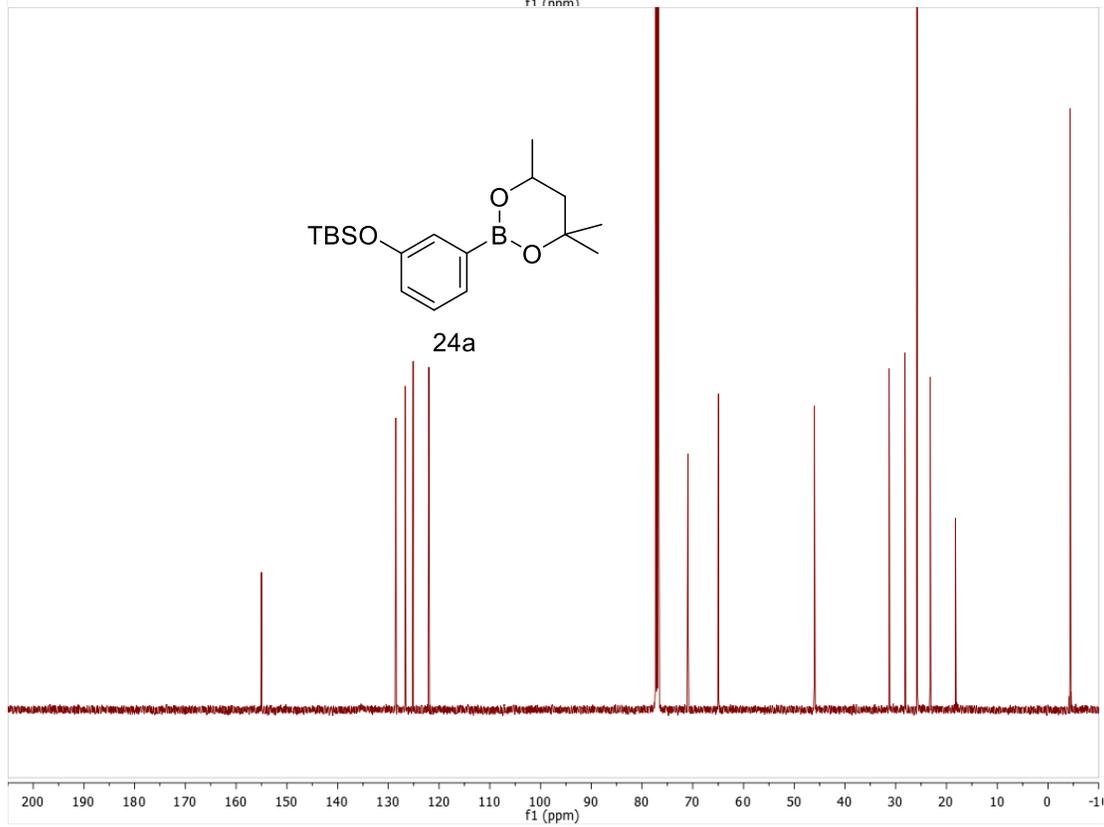
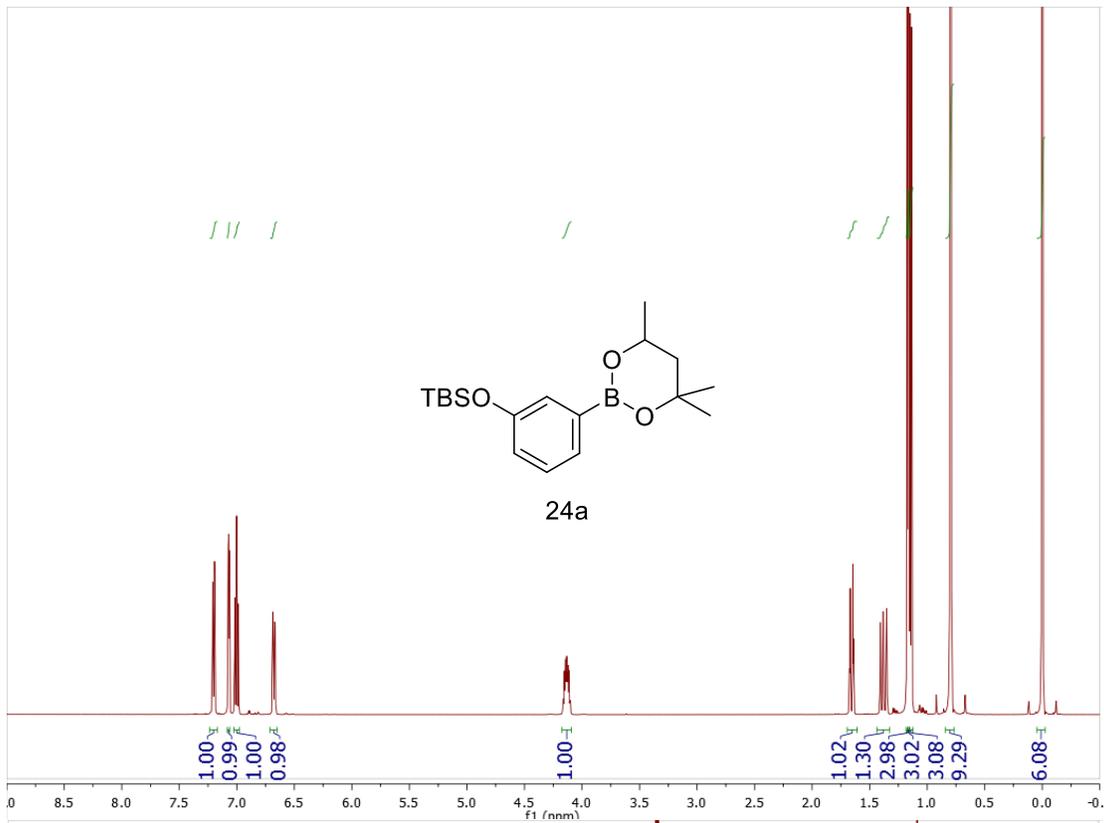


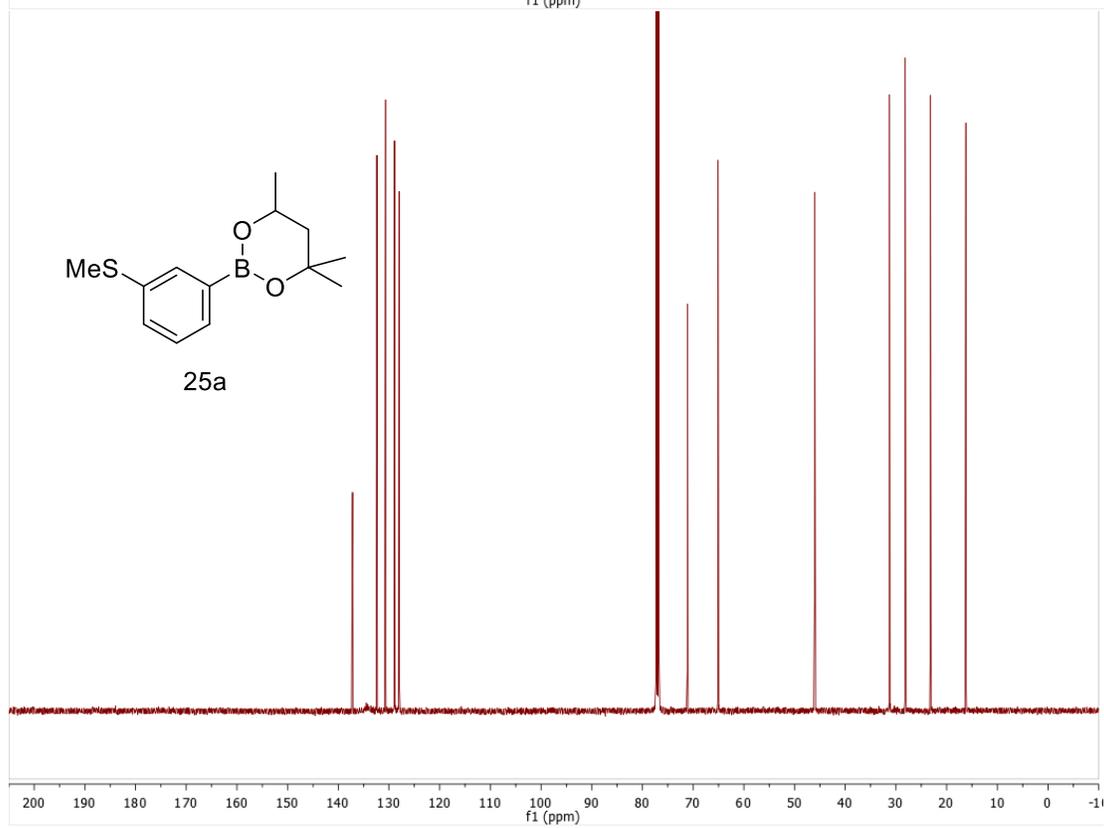
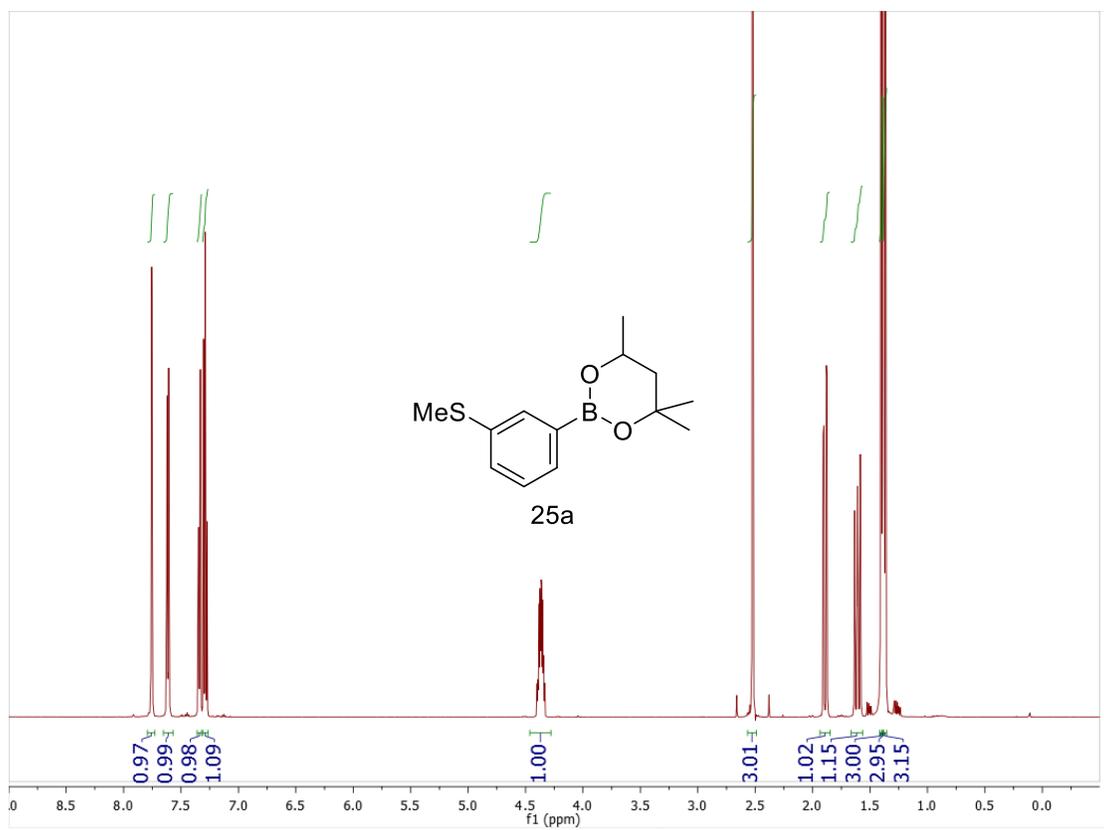


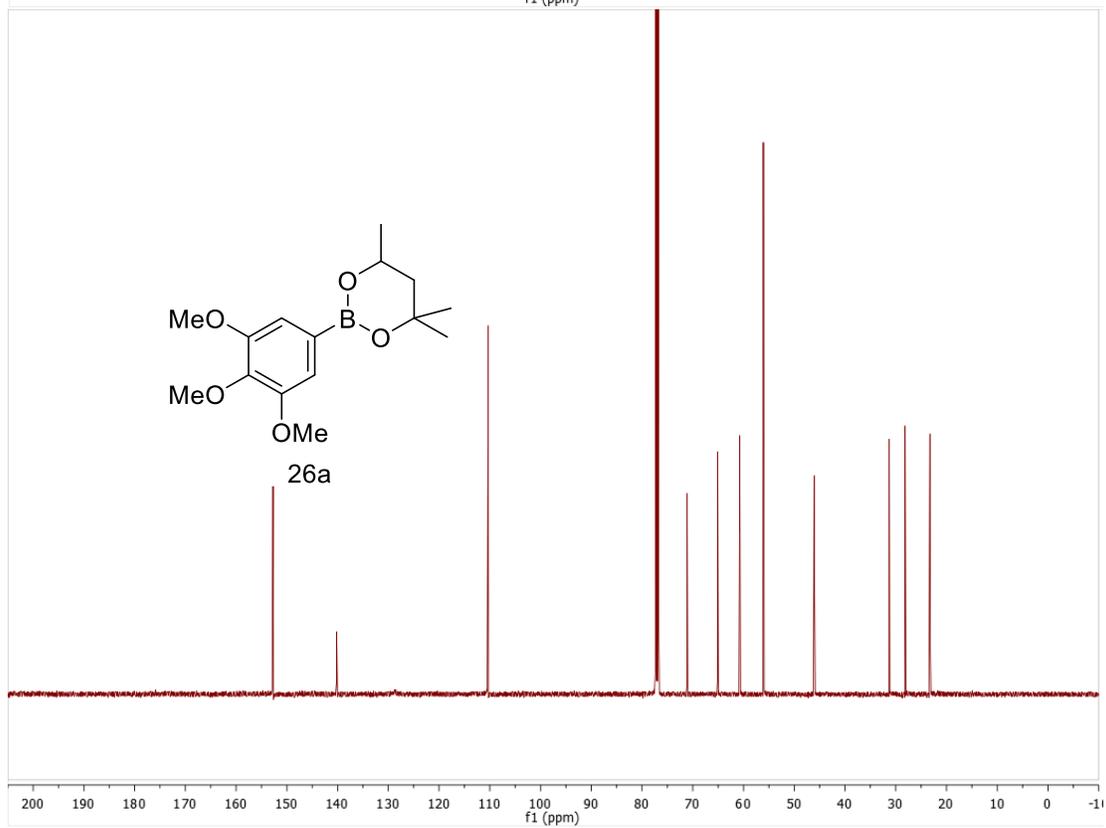
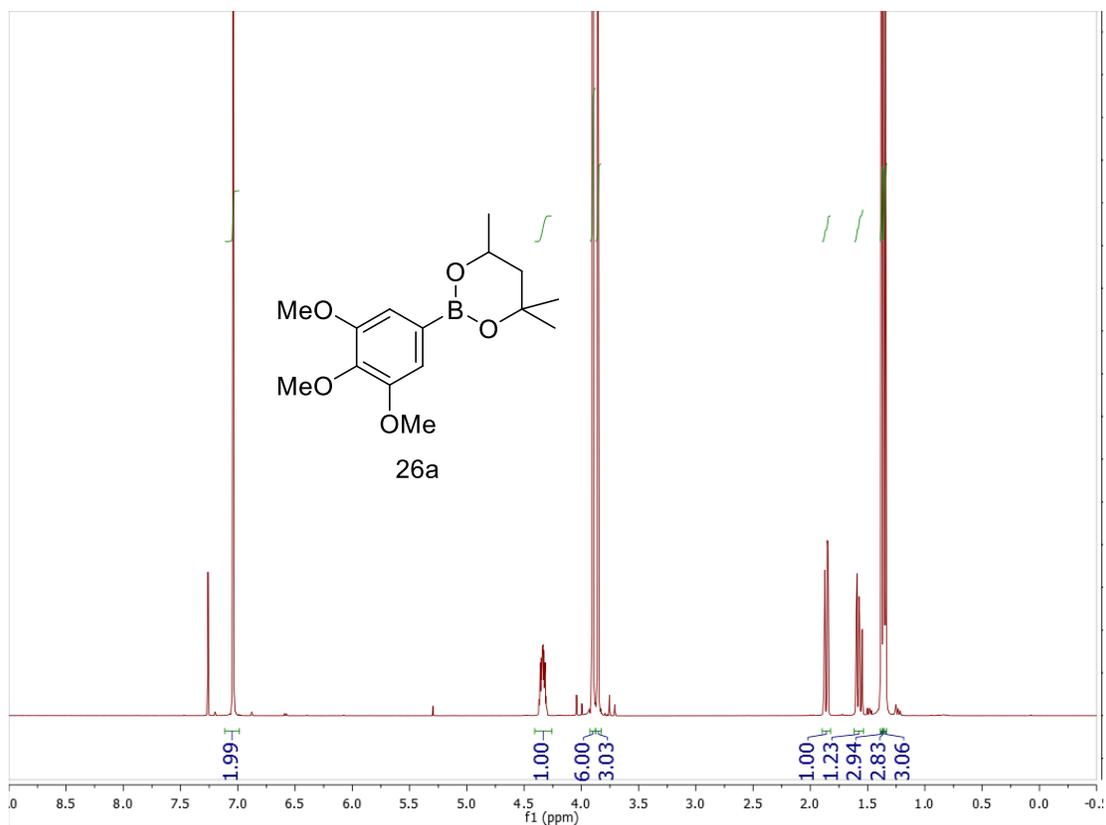


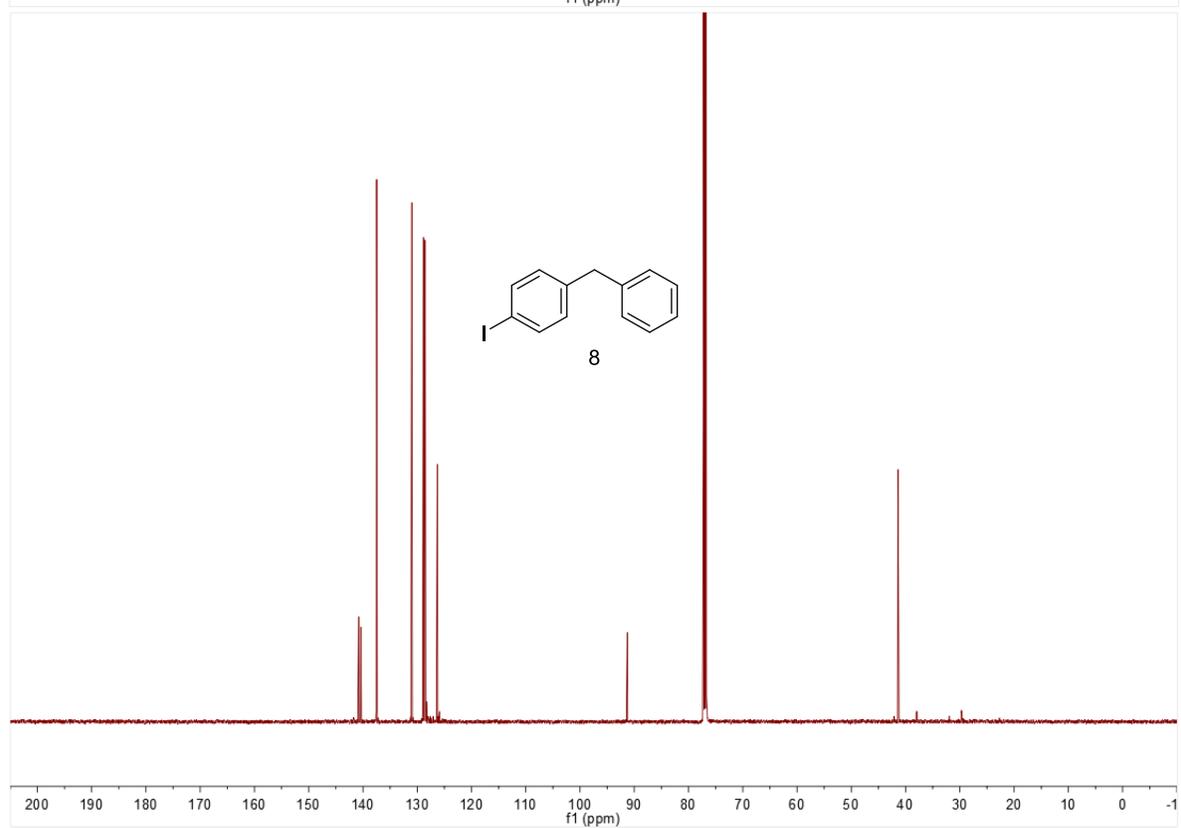
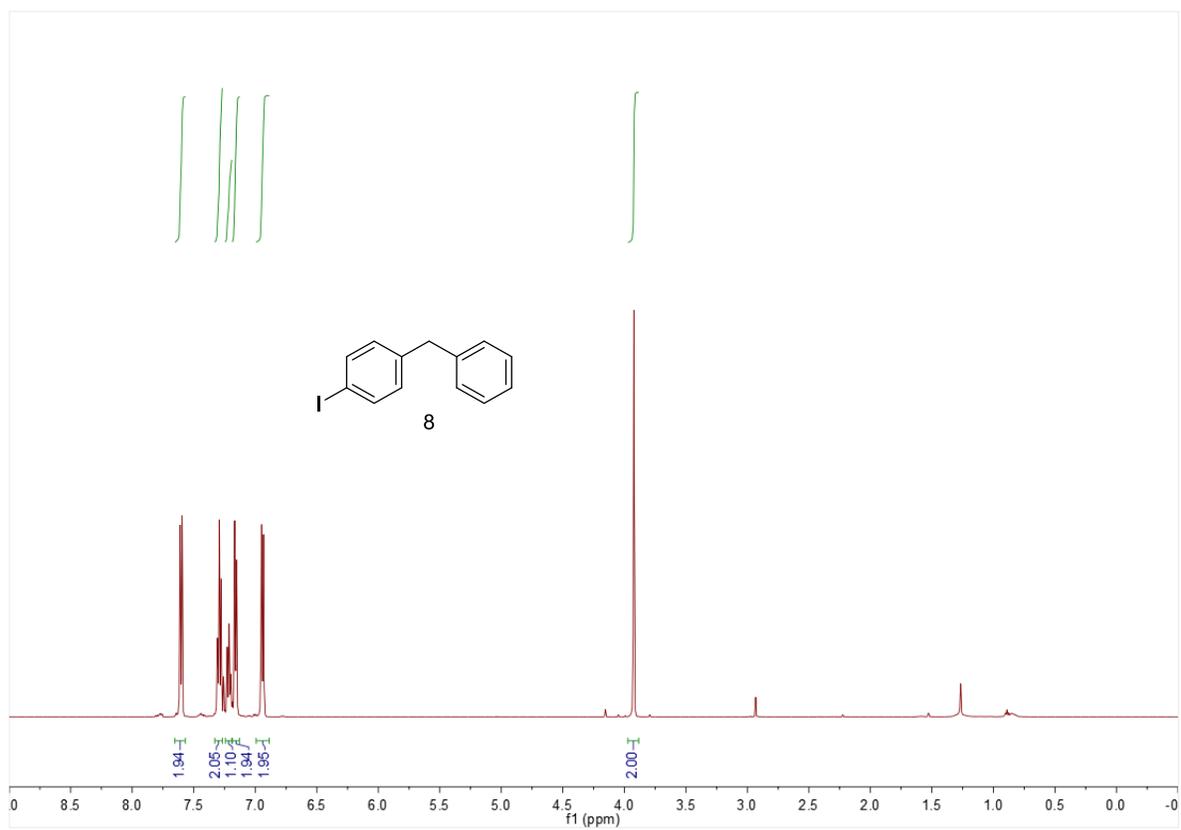


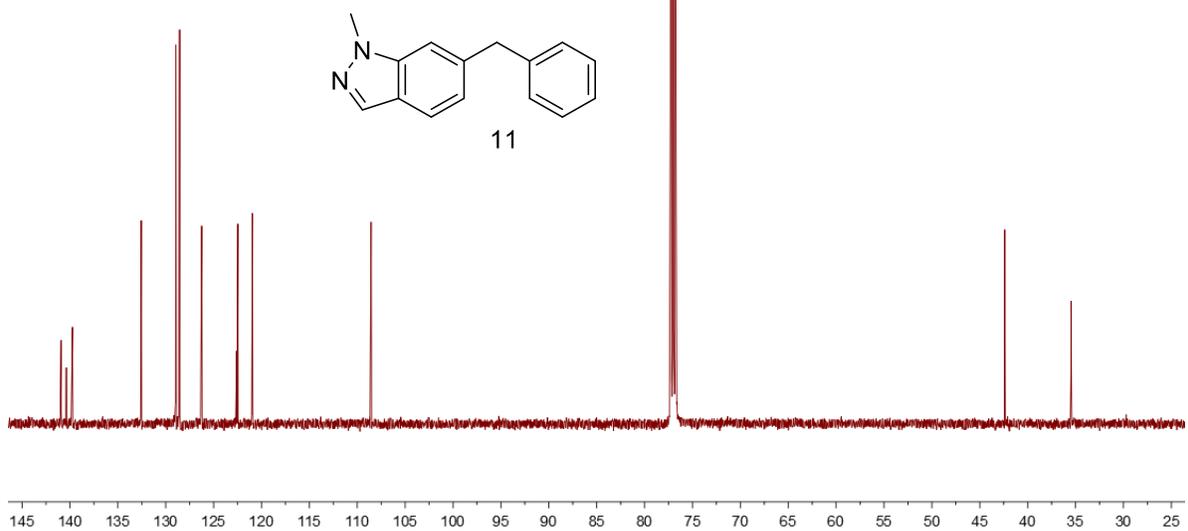
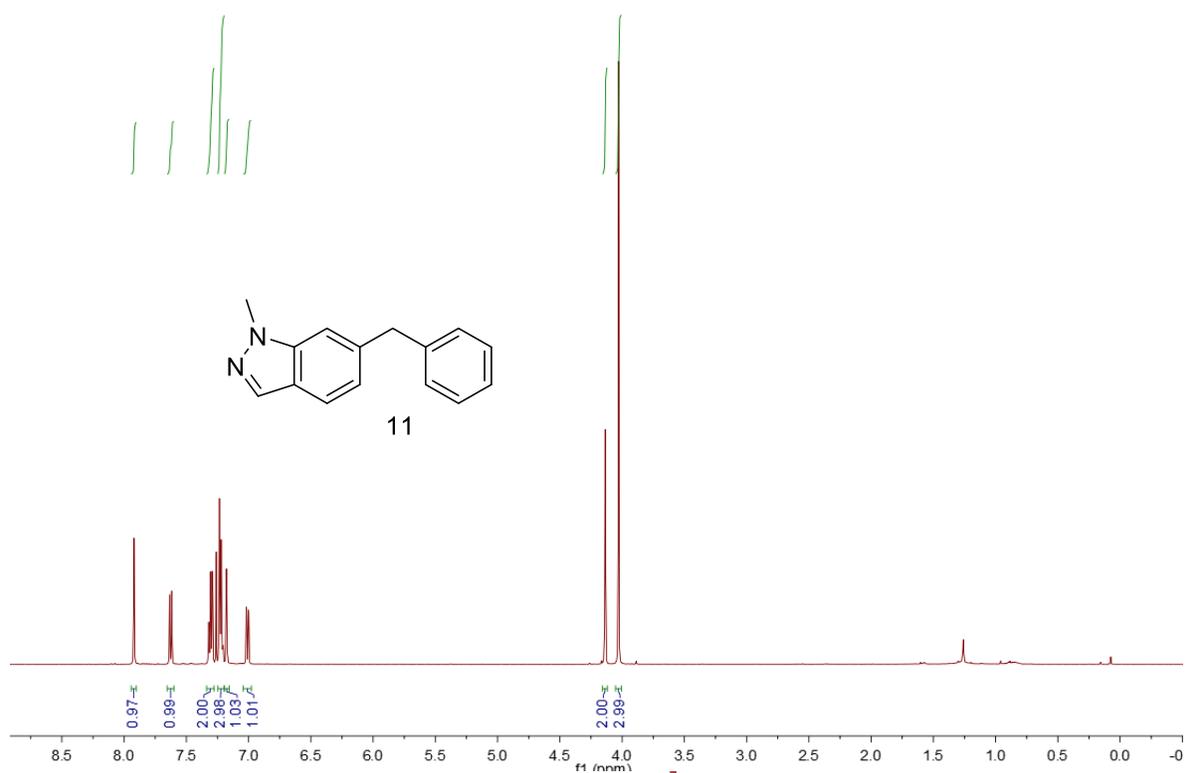


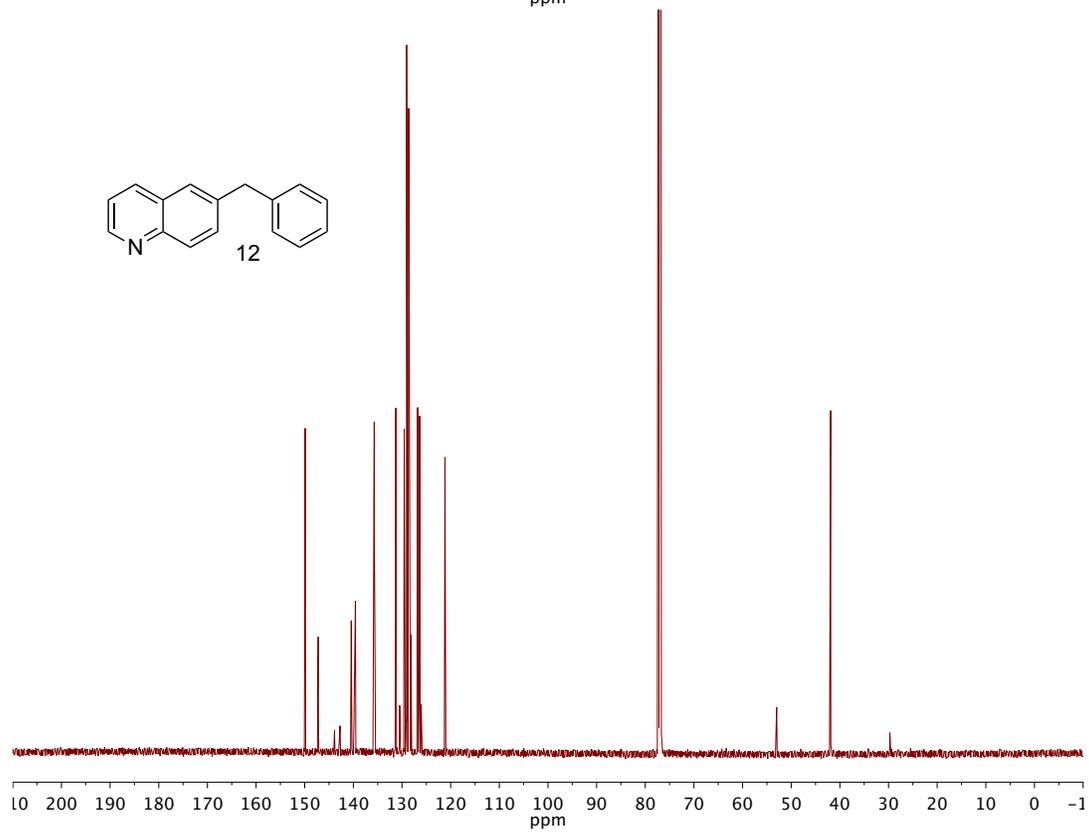
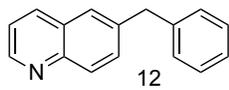
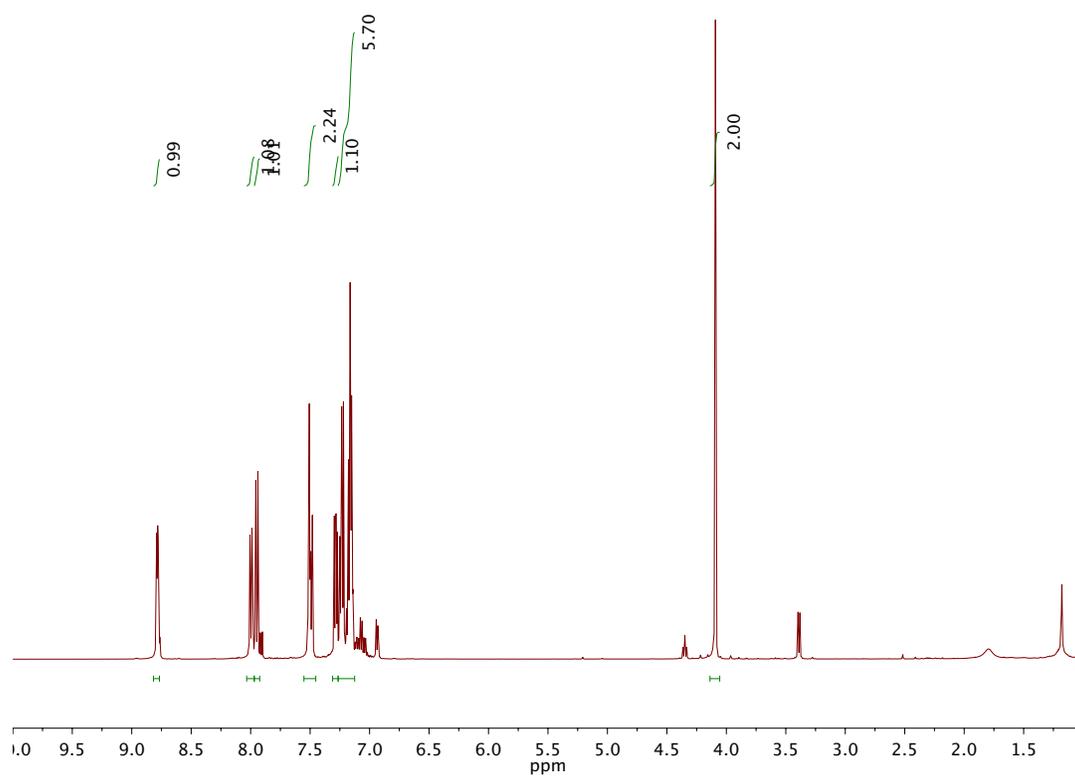


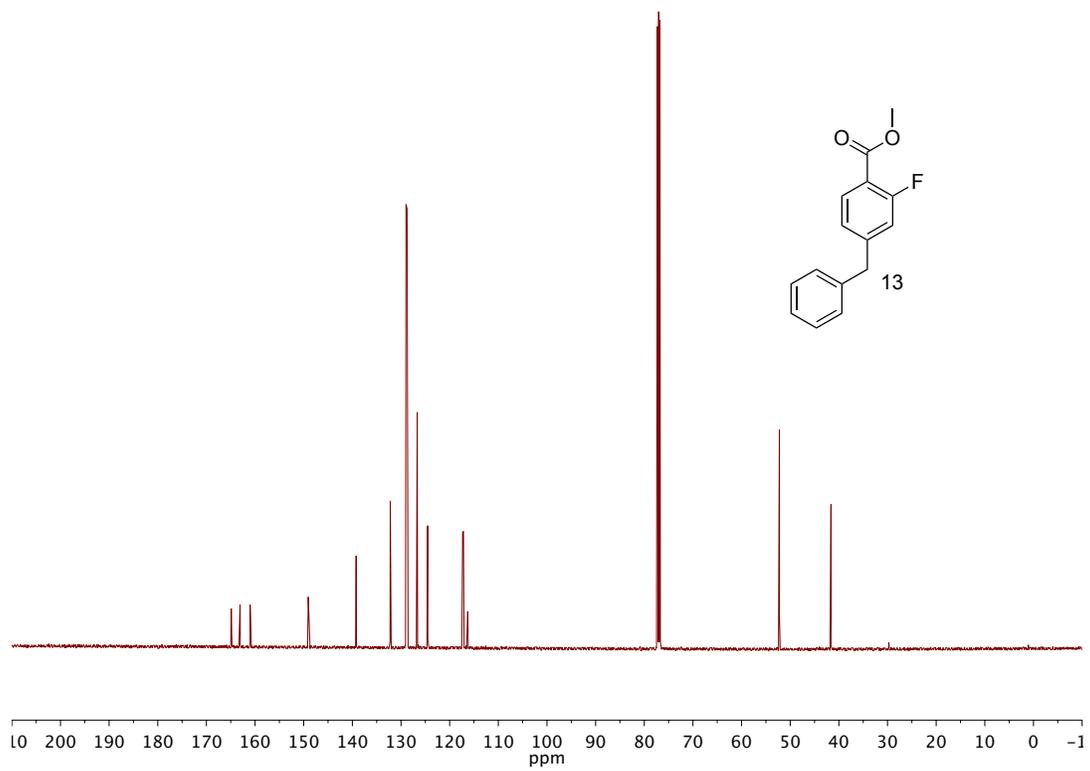
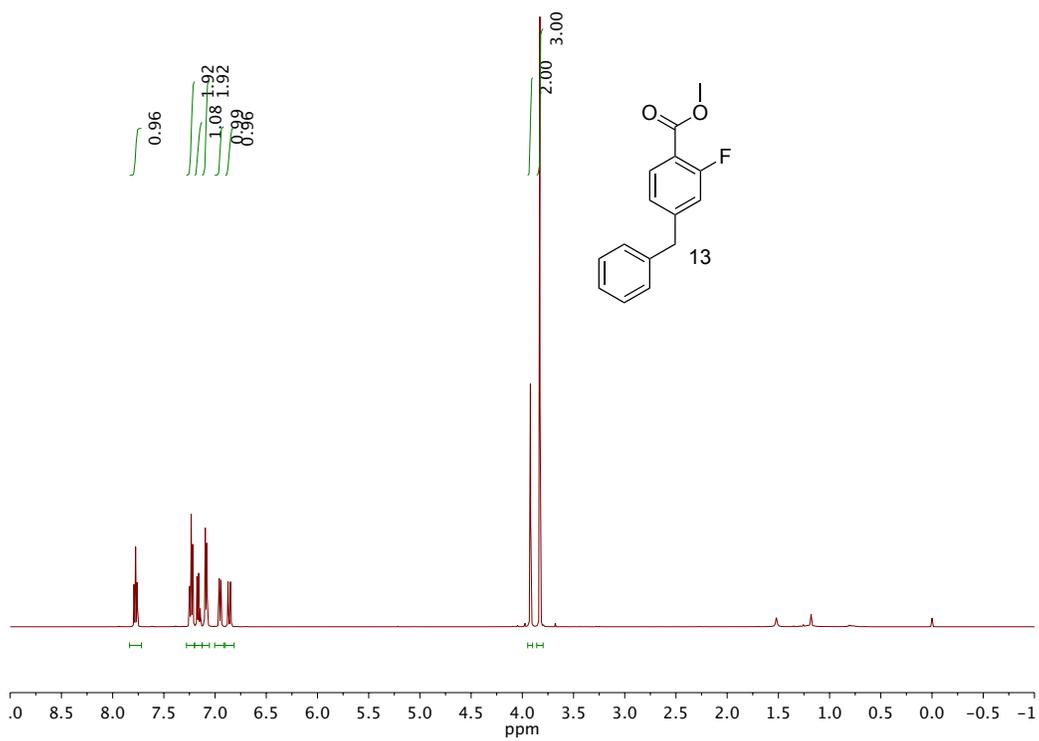


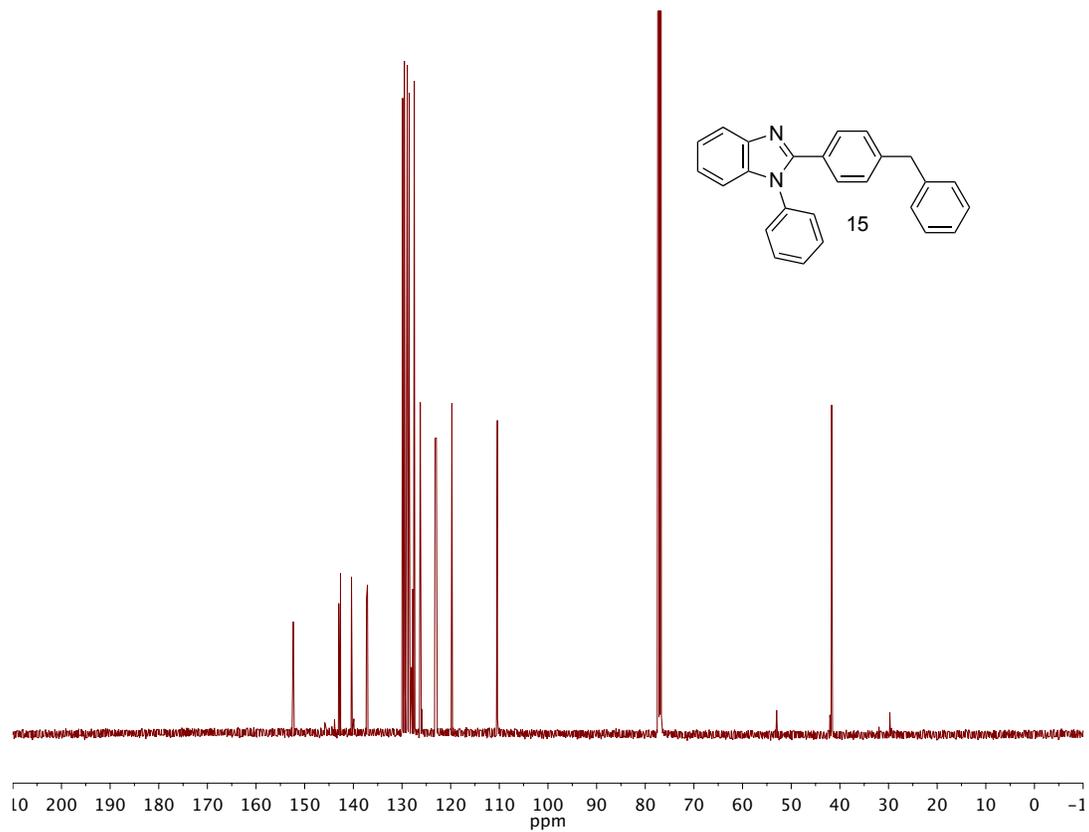
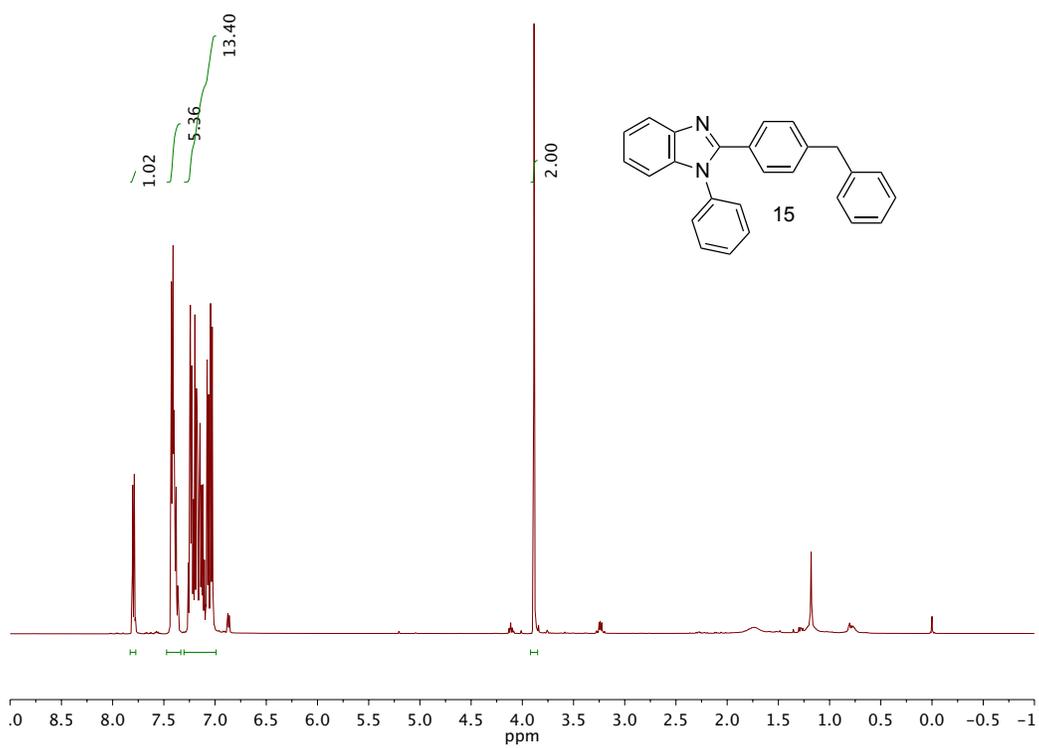


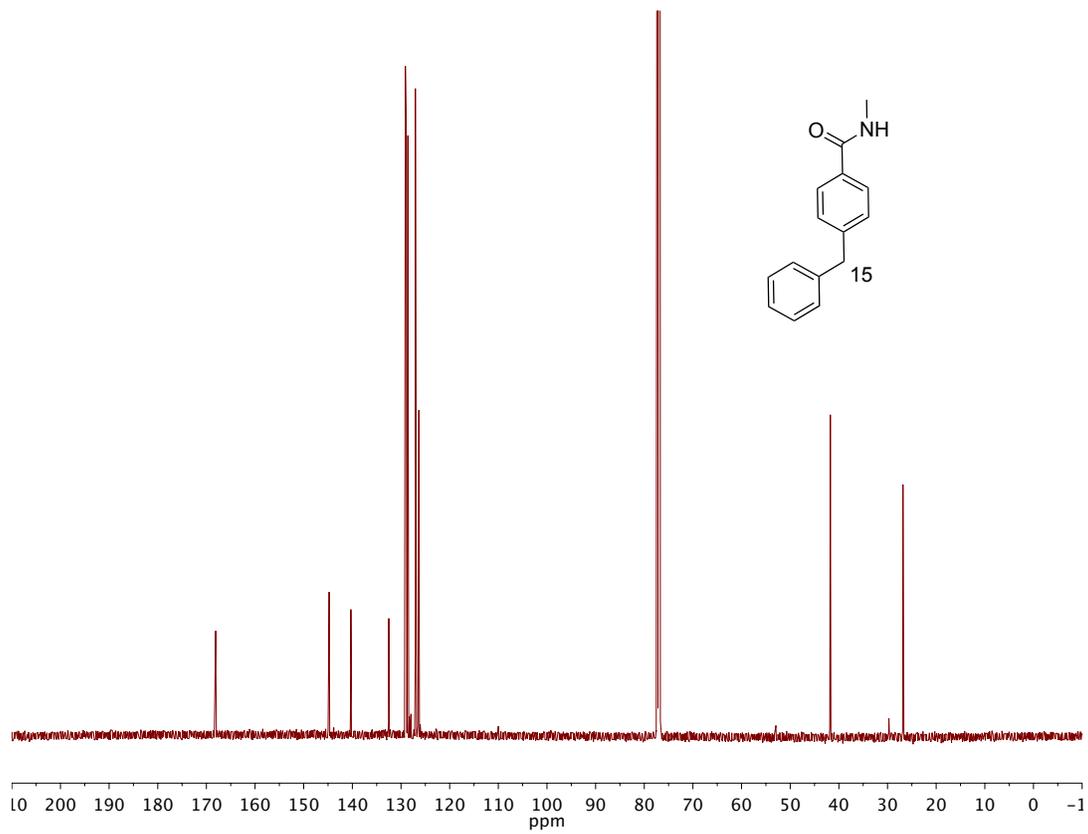
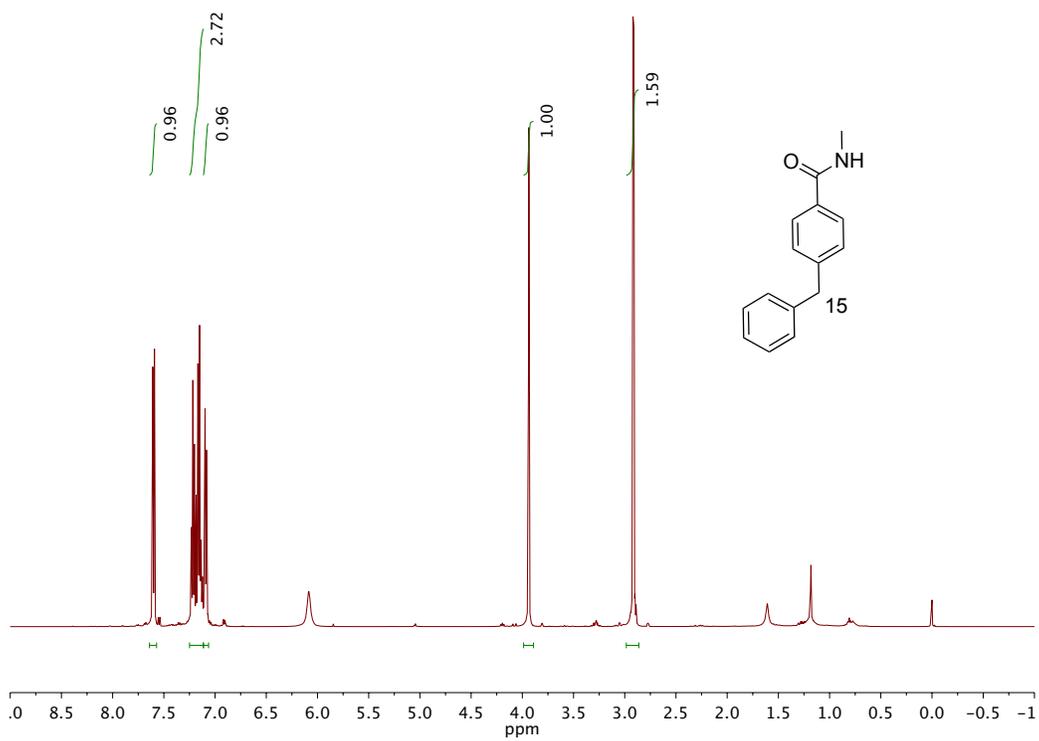


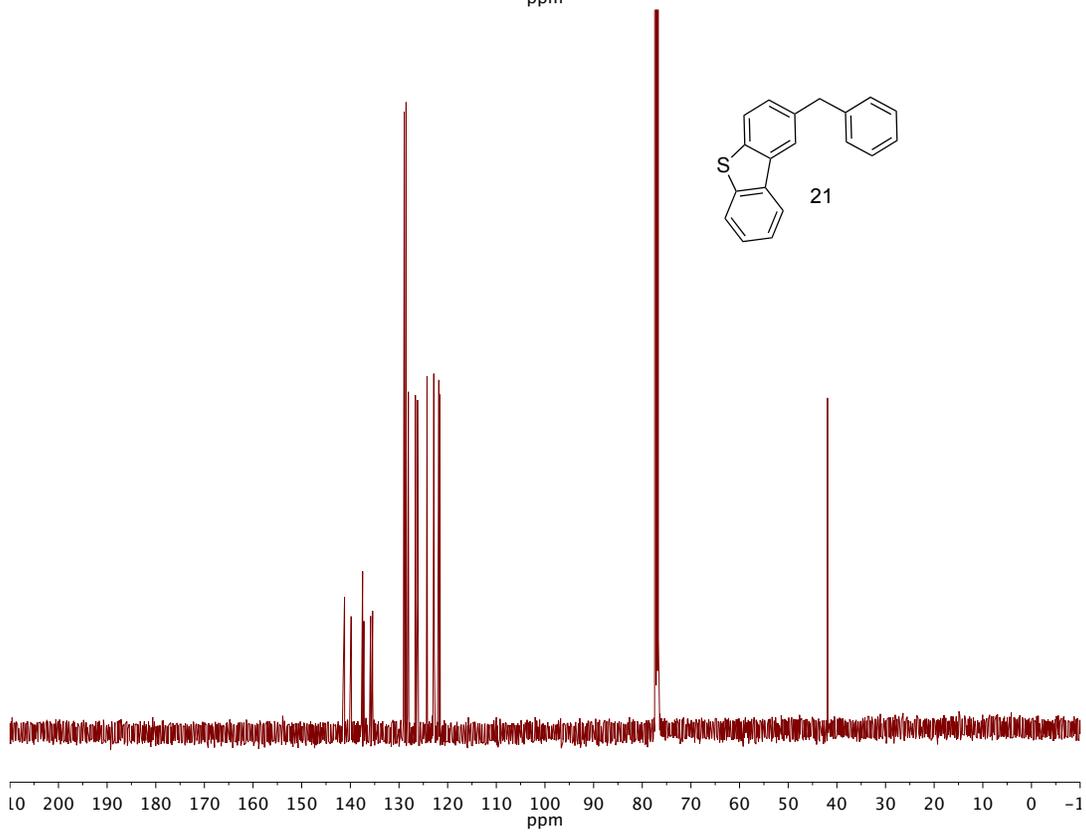
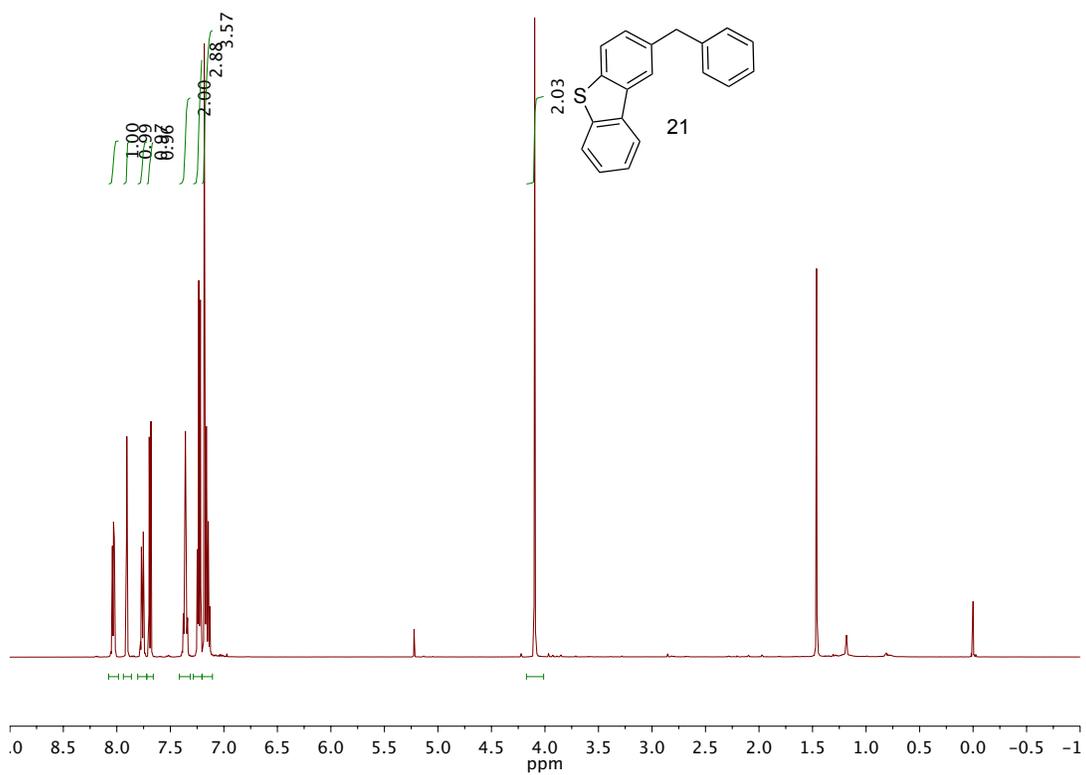


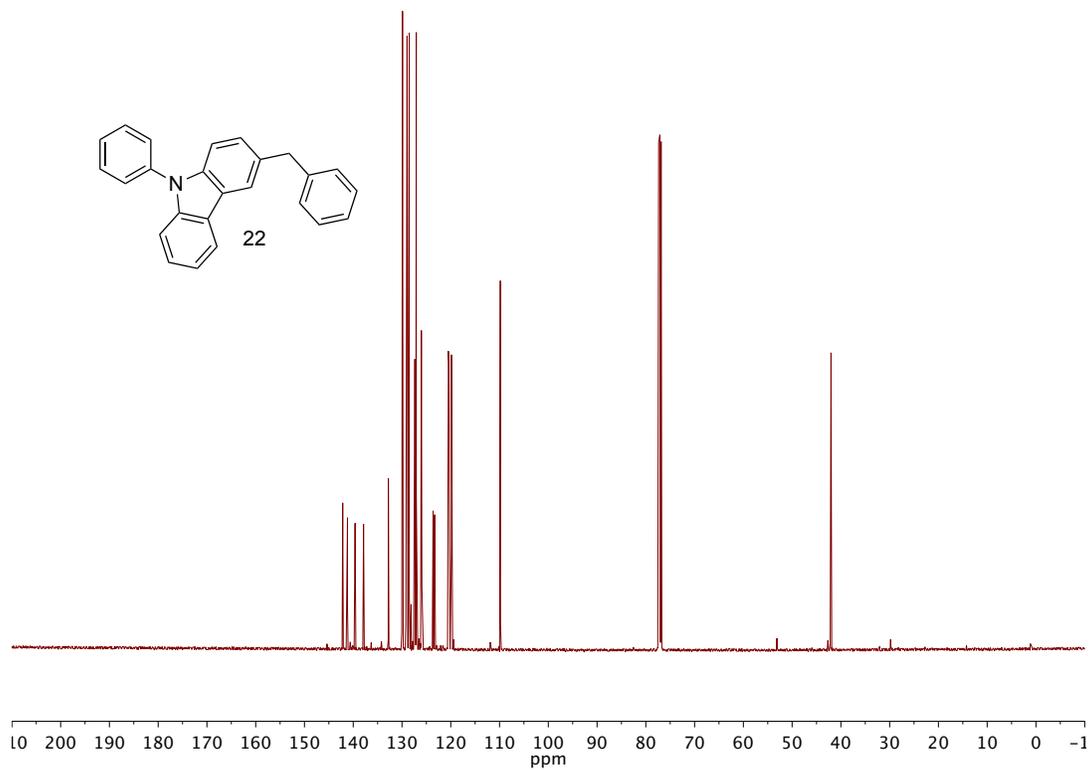
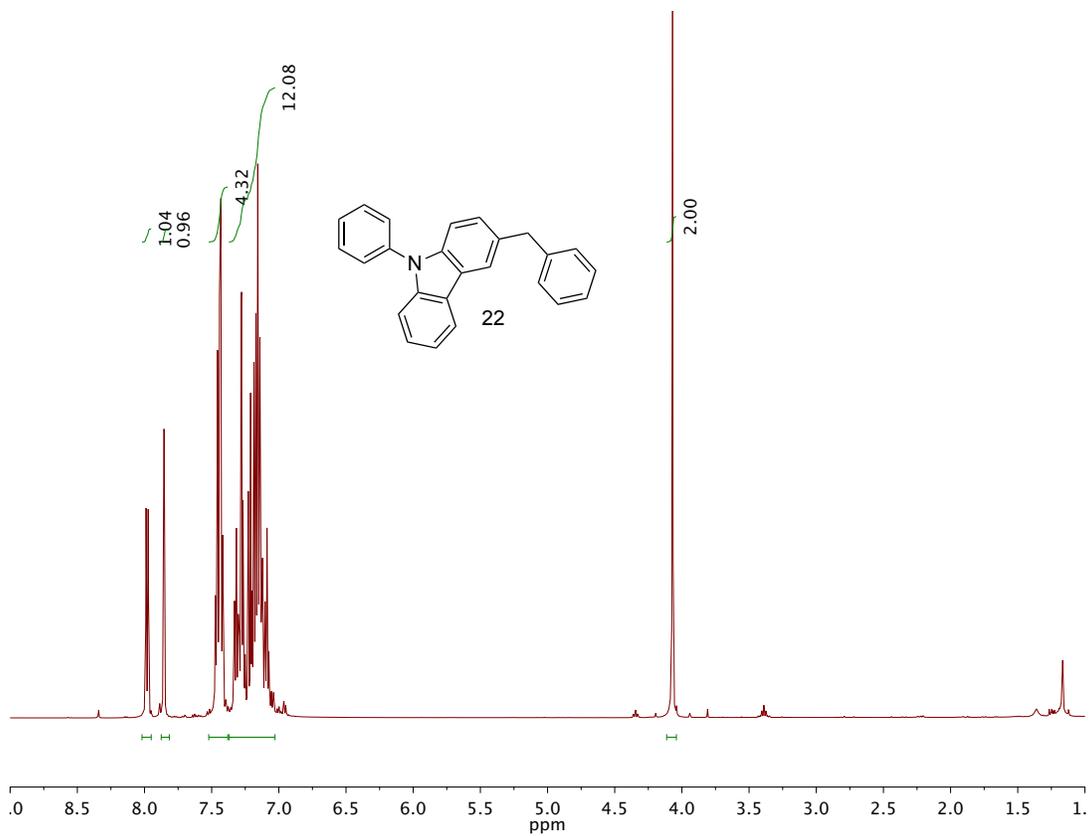


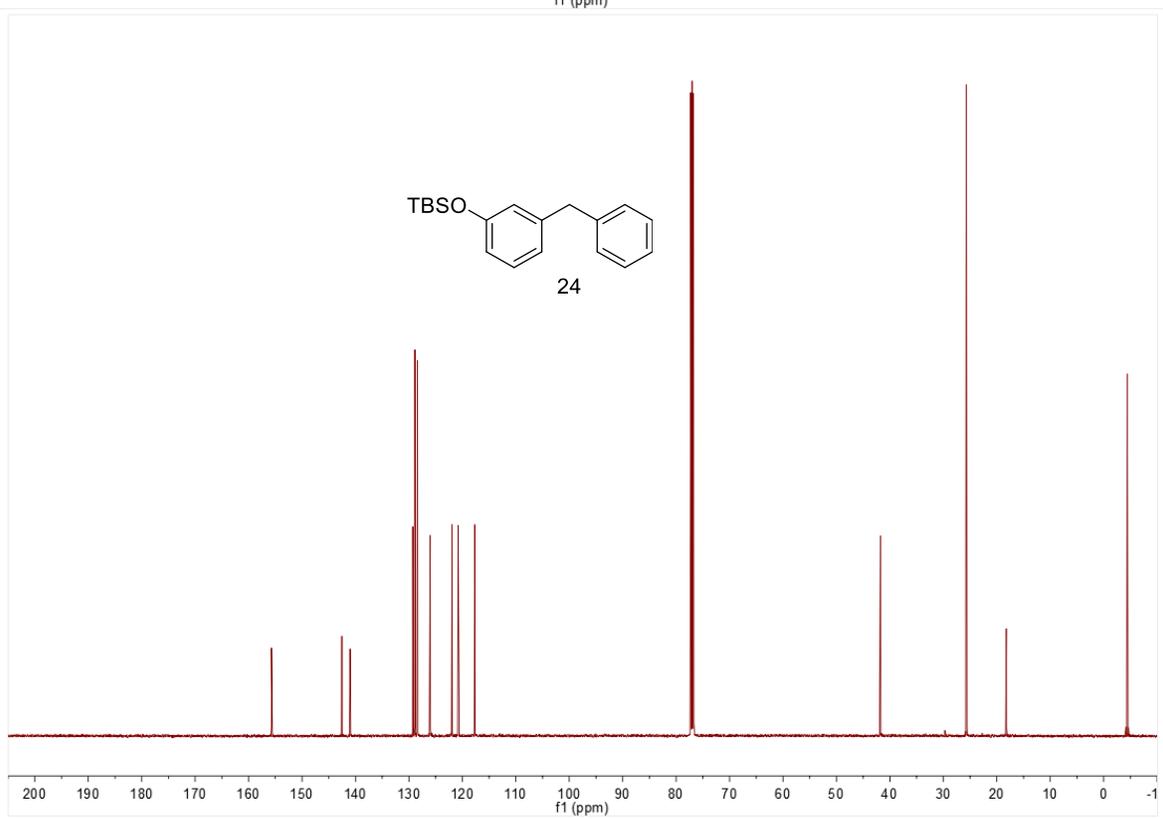
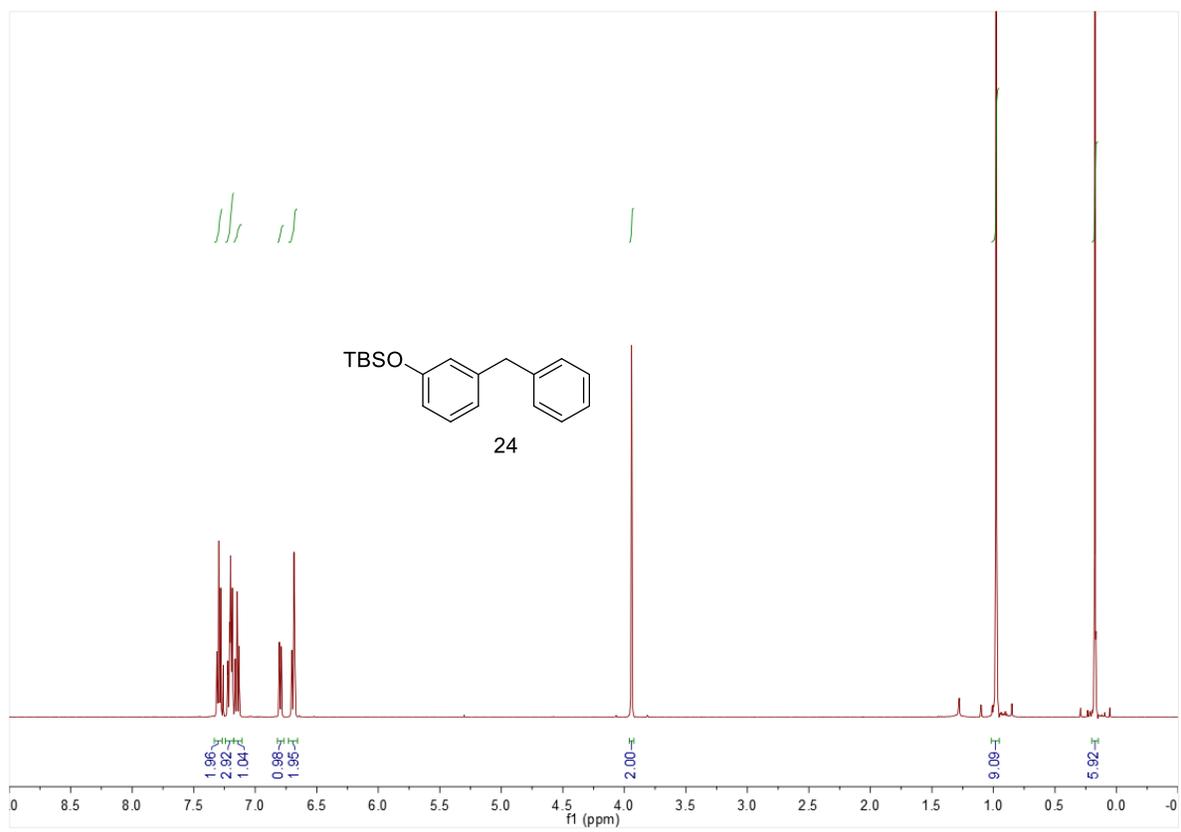


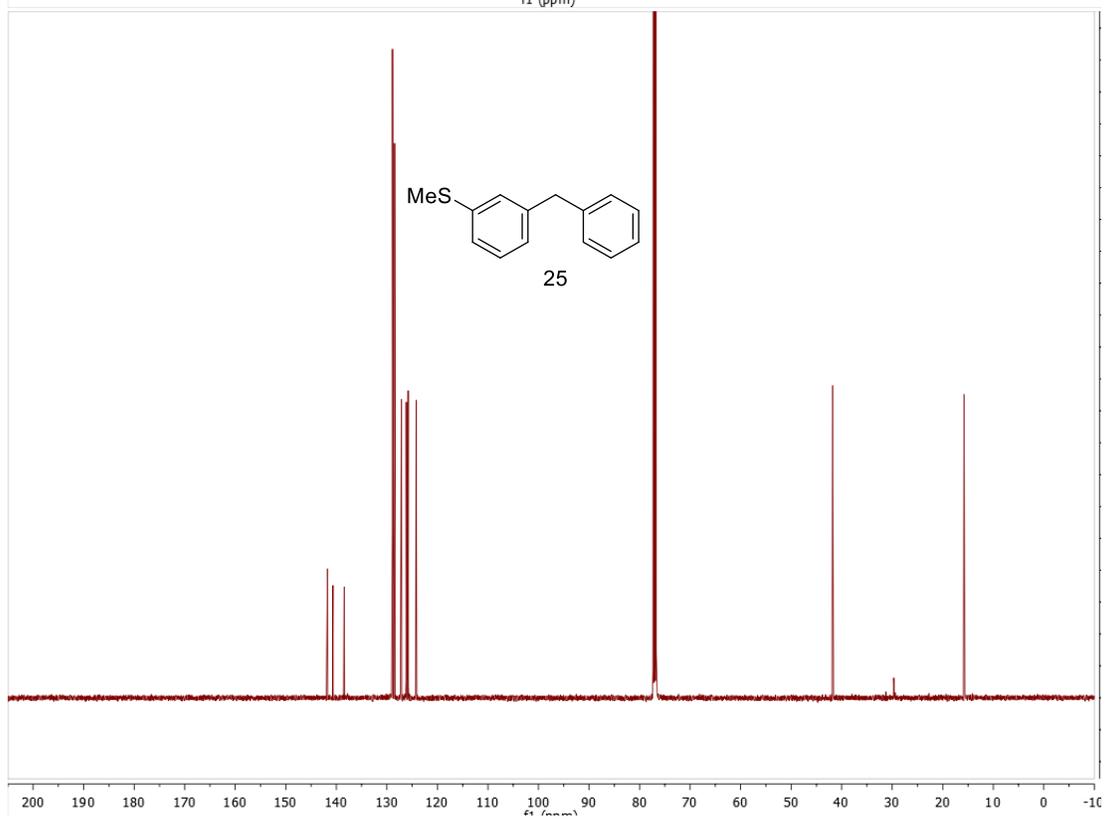
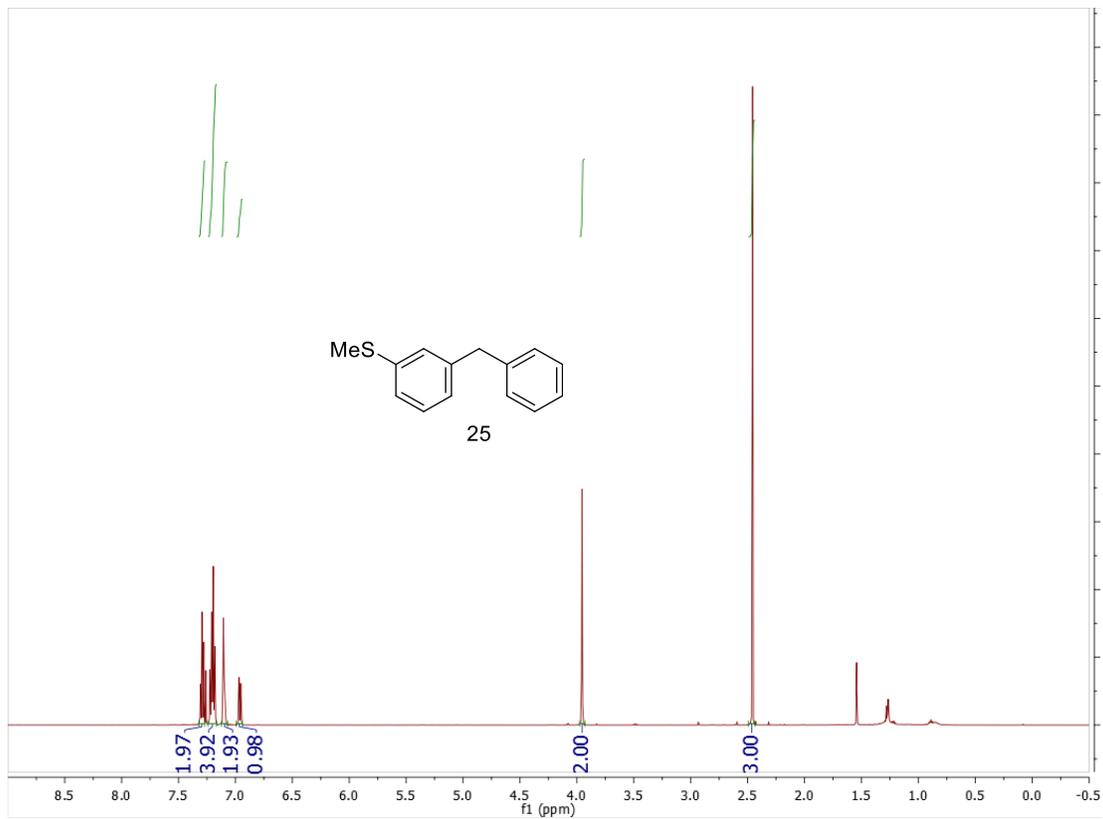


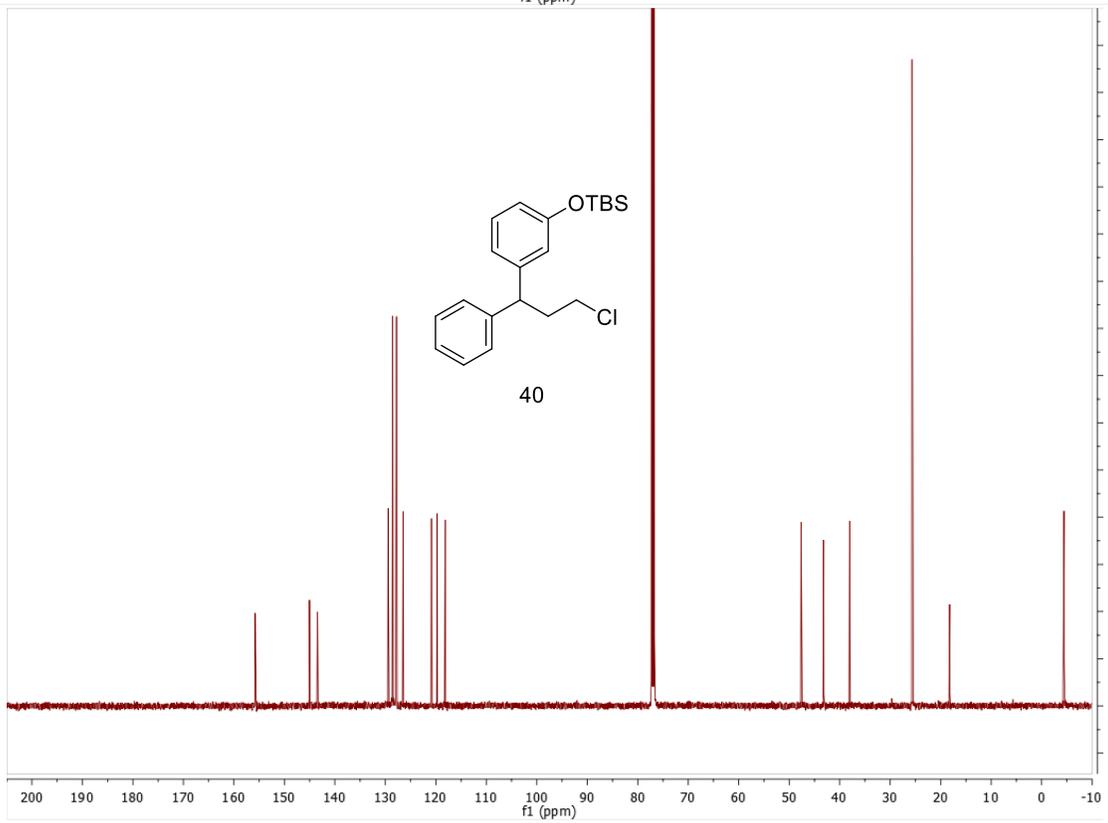
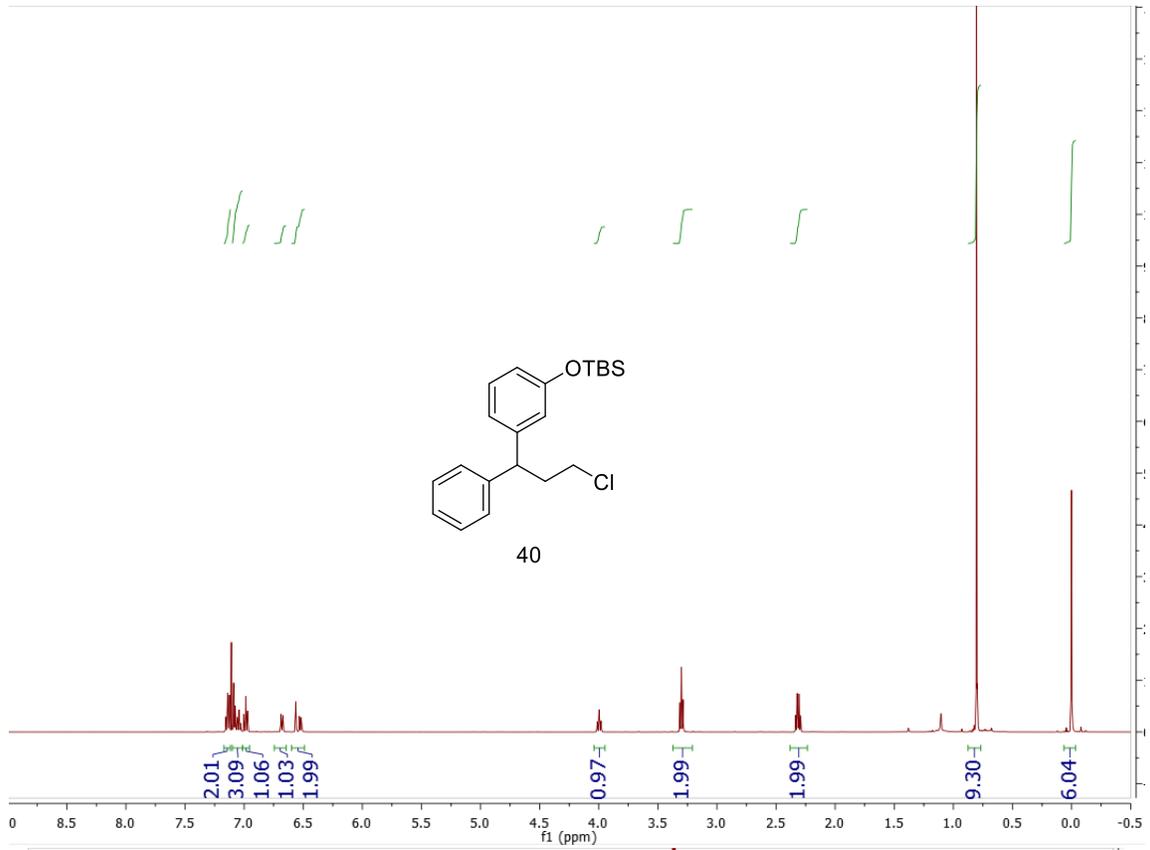


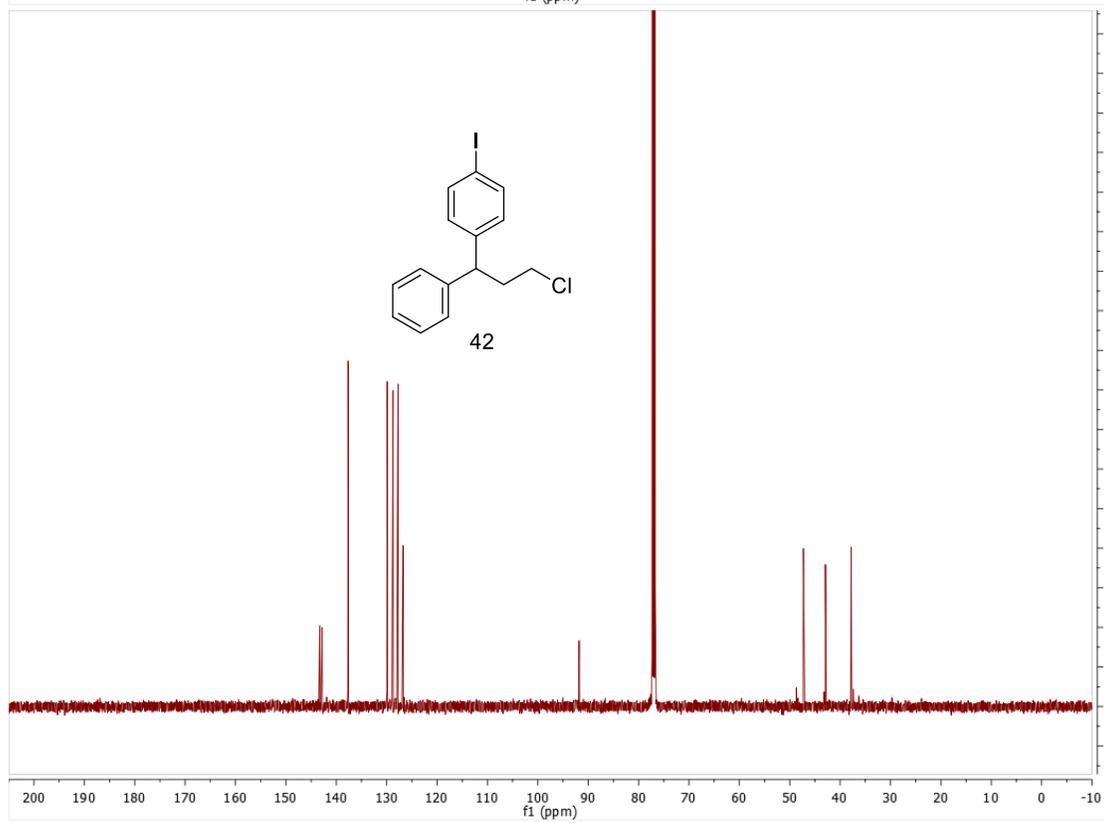
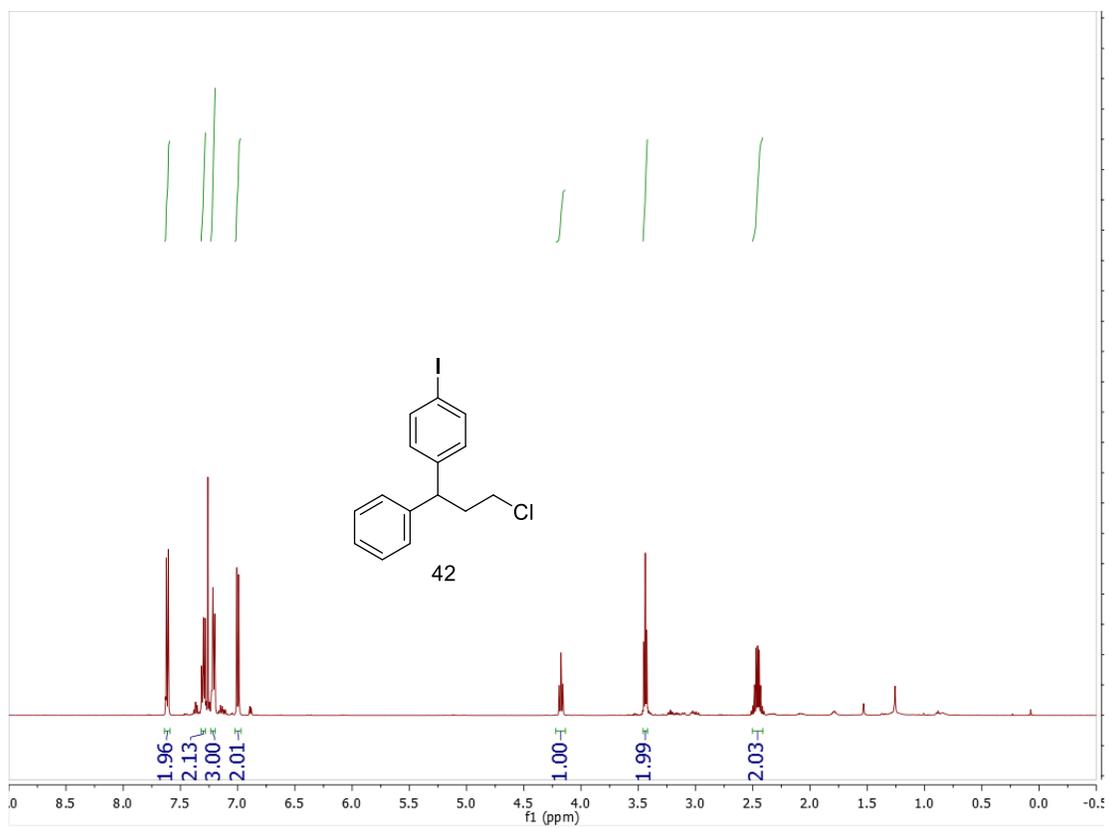


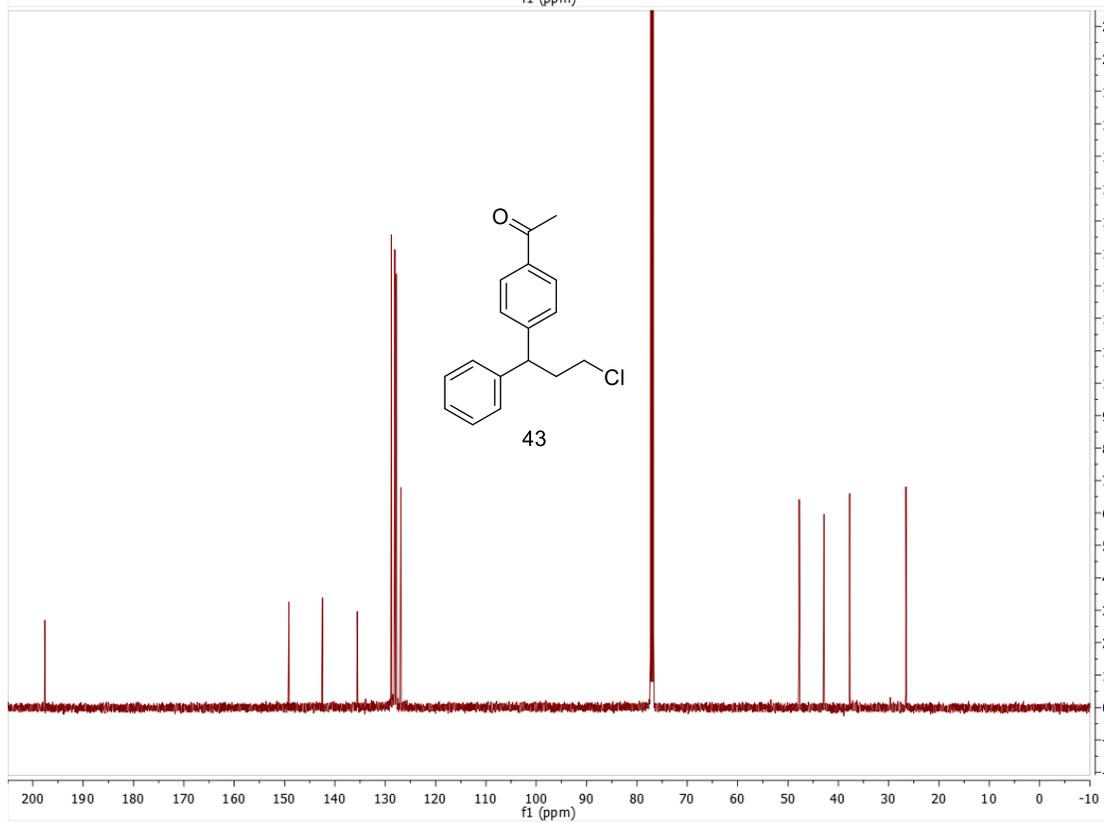
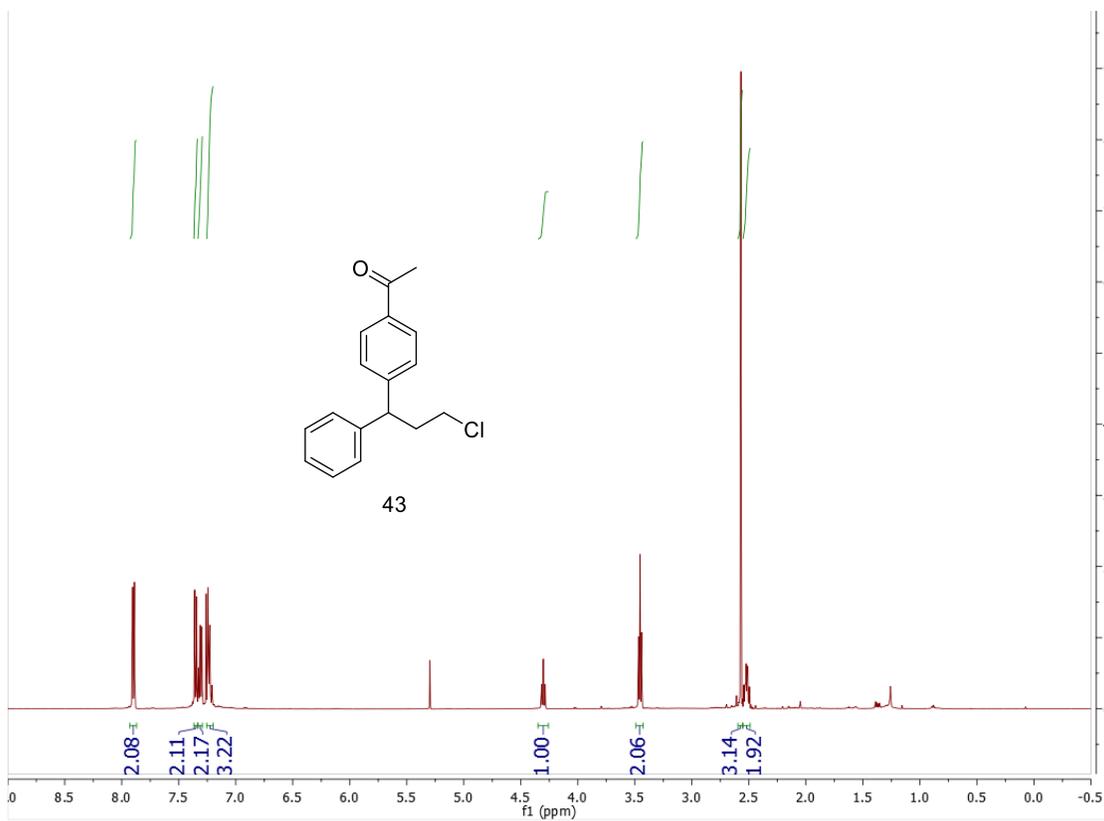












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